Chemical Consequences of Air Quality Standards

and of Control Implementation Programs

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ABSTRACT

The facilities available at the Statewide Air Pollution Research Center, University of California, Riverside, including the environmental chamber laboratory established under a joint California Air Resources Board (CARB)/University of California program, have been employed in several studies relevant to the development of air pollution control strategies by the CARB.

In order to assess the effects of potential emissions of nitrogenous species due to the proposed injection of ammonia into electric utility power plants (to reduce NO_x emissions), the atmospheric fates of selected nitriles (acetonitrile, propionitrile and acrylonitrile) were investigated. From a consideration of results of indoor chamber experiments and from our measurements of the absolute rate constants for the reaction of hydroxyl radicals with the nitriles, it is evident that the major atmospheric fates of these compounds will be via reaction with the OH radical. Additional dual-mode outdoor chamber experiments were carried out to ascertain the effects of emitted NH_3 on the NO_x-air and NO_x-HNO_3-air photochemical systems; no effect on the gas phase chemistry was observed, although higher particulate burdens were found on the added NH_3 sides.

In a continuing study of chamber-dependent effects, the magnitude and character of offgassing of nitrogenous compounds from the SAPRC 5800-liter chamber was determined under a variety of conditions. Subsequently a series of NO_x-air irradiations, with added traces of propane and propene to monitor OH radical levels, were carried out in four chambers of differing size to investigate the origin and nature of chamber-dependent radical sources. The results of this study showed conclusively the presence of unknown chamber-dependent radical sources, and indicated that photolysis of initial nitrous acid could be, at best, only a minor contributor to radical input during typical multi-hour chamber experiments.

In order to investigate the atmospheric fates of pesticides and herbicides, an exploratory study was carried out using long path Fourier transform infrared spectroscopy in a ~30,000-liter outdoor chamber with the selected model pesticide compounds, trimethylphosphate, phenyl N-methylcarbamate and 1,3-dichloropropene. Dark reactions with ozone and NO_x-air photooxidations were carried out. For all three compounds, reaction with the OH radical will be the major atmospheric loss process, with lifetimes calculated to be in the range of ~20-50 hours.

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I. EXECUTIVE SUMMARY

This report presents results from several projects of direct relevance to the development and implementation of air pollution control strategies by the California Air Resources Board. In two new areas of research, we have (a) investigated the atmospheric chemistry of selected nitrogenous compounds (acetonitrile, propionitrile and ammonia) which might be expected to be products of the injection of ammonia in fossil fuel power plants (in order to reduce NO_x emissions), including the determination of absolute rate constants for the reactions of OH radicals with selected nitriles, and (b) have conducted exploratory studies, employing long-path Fourier transform infrared spectroscopy, to determine the atmospheric fates of selected pesticides and related model compounds.

As part of an on-going program to obtain a reliable data base for the validation of the chemical mechanisms in urban airshed models utilized by the Air Resources Board, we have experimentally investigated chamber-dependent radical sources using four SAPRC chambers of differing size and employing differing light sources (i.e., 5800-liter TFE coated evacuable chamber, 6000-liter indoor all-Teflon chamber, ~100-liter Teflon bags and ~40,000-liter outdoor Teflon bags). Our results, which conclusively show the presence of chamber-dependent radical sources, have significantly advanced our understanding of this phenomenon, and have important implications concerning computer models of photochemical air pollution based on smog chamber data as well as for experimental determinations of hydrocarbon reactivity in chambers.

Summaries of the results obtained for each element of this research program (Contract No. A8-145-31) are given in the following pages of the Executive Summary. Sections II-V provide a detailed report of the work carried out in the studies cited above. Appendix A provides the detailed data sheets for the experiments relating to the chamber radical source investigation.

A. Investigation of the Atmospheric Reactions of Nitrogenous Compounds Anticipated from NH_3 Injection in Electric Utility Power Plants

The amount of NO and NO_2 formed from the oxidation of the nitrogen in air during the burning of fossil fuels can be significantly reduced by modifications to combustion technology, but such modifications have little effect on the formation of NO_x resulting from the oxidation of fuel-bound nitrogen. On the other hand reduction of NO by ammonia (NH_3) injection has been proposed as a viable method for control of the NO_x formed from both sources in the effluents of fossil fuel burning power plants. At present ammonia appears to be the only compound that is capable of selectively reducing NO_x in the presence of a large amount of oxygen over a wide range of NH_3/NO molar ratios, and research has been undertaken in both the U.S.A. and Japan to perfect ammonia injection methods employing both catalytic and noncatalytic (e.g., Exxon's Thermal Denox process) techniques.

Pending regulations in California call for approximately 95% reduction in NO_x emissions from sources such as electric utility power plants by 1985. Under the impetus of this requirement serious consideration is being given to application of the Thermal Denox process to power plants in the South Coast Air Basin, and perhaps elsewhere in the state. Hence it is important to establish now whether or not significant emissions of NH_3 may occur, and whether, as a result of the complex free radical reactions involved in this process, other compounds may be formed which in themselves may constitute a hazard or which under atmospheric transformations may lead to the formation of toxic species.

In preliminary laboratory studies Exxon workers have identified only five species as pollutant by-products from the Thermal Denox process: N_2O, CO, HCN, SO_3 and NH_4HSO_4. In addition they found that ammonia itself will be emitted at a concentration of at least 5 ppm. However, consideration of actual power plant operating conditions of temperature and oxygen concentration together with available kinetic and thermodynamic data suggested the possibility (Brown 1979) that a number of low molecular weight nitrogenous compounds including alkyl amines and nitriles might be formed at significant concentration levels.

Atmospheric Reactions of Selected Nitriles. The California Air Resources Board funded a program in the laboratories of Professor Robert Sawyer at the Department of Mechanical Engineering, University of California, Berkeley, to attempt to detect the formation of nitrogenous compounds under laboratory conditions. While the intention was to use the data from this UC Berkeley study to determine which nitrogenous species to study at SAPRC, it was not possible to postpone this phase of the SAPRC study until the Berkeley data became available. Hence, based upon the available information it was decided to investigate the atmospheric reactions of selected aliphatic nitriles: acetonitrile (CH_3CN), propionitrile (C_2H_5-CN) and acrylonitrile ($CH_2=CHCN$). These studies were carried out in two parts: (a) environmental chamber studies of the reactions of these compounds with ozone and the nitrate radical (NO_3), and in irradiated NO_x-air systems; (b) the determination, using a flash photolysis-resonance fluorescence technique, of the absolute rate constants for the reaction of OH radicals with these three nitriles. In addition, we investigated, using an outdoor chamber in dual-mode, the effect of NH_3 on radical levels from NO_x-air irradiations in order to assess the impact of NH_3 emissions on photochemical air pollution systems.

The studies to investigate the major atmospheric fates of the nitriles CH_3CN and C_2H_5CN were carried out in the SAPRC ~6400-liter indoor all-glass (Pyrex) environmental chamber. The first set of experiments were carried out to determine the dark decay rates of acetonitrile and propionitrile in pure air in the presence and absence of O_3 and NO_x, and consisted of the following: (1) injection of ~100 ppb of each nitrile into an atmosphere of pure air, and monitoring its decay; (2) injection of 1.5 ppm of O_3 into the chamber where ~100 ppb of each nitrile has already been injected; and (3) injection of ~0.5 ppm of NO_2 into the chamber containing ~100 ppb of each nitrile and ~1.5 ppm of O_3.

The purpose of the third experiment was to determine if the nitriles react with the nitrate (NO_3) radical which is formed from the reaction of O_3 with NO_2. This possibility had to be examined because we have previously shown (Carter et al. 1981) that reaction with the NO_3 radical is a significant atmospheric degradation pathway of phenolic compounds.

No significant decay of either nitrile, other than that which can be attributed to dilution due to sampling or chamber leakage, was observed under any of the conditions employed. Thus, removal of these simple nitriles (CH_3CN and C_2H_5CN) by surface absorption, by reaction with O_3, or by reaction with the NO_3 radical will be negligible under atmospheric conditions.

From these observed nitrile loss rates in the 6400-liter environmental chamber, upper limits to their rate constants for reaction with O_3 can readily be calculated to be:

$$O_3 + CH_3CN; \quad k < 1.5 \times 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$$

and

$$O_3 + C_2H_5CN; \quad k \leq 1.0 \times 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$$
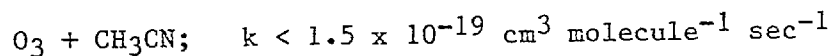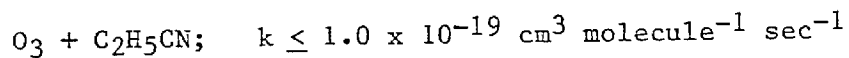
at 299 ± 1 K.

For the case of acrylonitrile ($CH_2=CHCN$), an upper limit to the ozone reaction rate constant has recently been determined in another study from the decay of O_3 in the presence and absence of $CH_2=CHCN$ to be $k \leq 1.0 \times 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$ at 296 ± 2 K (Atkinson et al. 1981).

In order to determine the loss rates of the nitriles due to photolysis and/or reaction with the hydroxyl radical ~200 ppb of CH_3CN and ~100 ppb of C_2H_5CN were irradiated in (a) pure dry air and (b) NO_x-dry air, with < 100 ppb of neopentane and n-butane added as tracers to monitor chamber OH radical levels.

In both irradiations, the nitriles and the two alkane tracers were observed to disappear at rates somewhat higher than anticipated from the sampling rates. The observed differences in the disappearance rates of neopentane and n-butane implies the presence of OH radicals, and the OH radical concentration was accurately determined from analysis of the neopentane/n-butane concentration ratio data (Atkinson et al. 1978), since this procedure eliminates gas chromatographic sample size differences. With these radical levels the disappearance rates of neopentane and n-butane due solely to reaction with OH radicals were then calculated allowing a chamber dilution rate of $(7-8) \times 10^{-4} \ min^{-1}$ to be estimated for both irradiations. Since the nitrile disappearance rates were, within

experimental error, identical to this derived dilution rate, no evidence of photolytic or chemical reaction loss rates could be obtained, in agreement with the nitrile-pure air photolysis.

To obtain further quantitative information as to the OH radical reaction rate constants, absolute rate constants were obtained using the flash photolysis-resonance fluorescence technique available at SAPRC.

Using this technique, which has been described in detail previously in the literature (Harris et al. 1980), the rate constants k for the reaction of OH radicals with the nitriles CH_3CN, C_2H_5CN and $CH_2=CHCN$ (acrylonitrile) given in Table 1 were determined. In the case of acrylonitrile decay rates were also measured at total pressures of 100 and 500 torr of argon at 298 K. As can be seen from and Table 1, the rate constant was ~18% higher at the highest pressure indicating that the reaction proceeds partially or entirely via an addition mechanism and that at room temperature the reaction is in its fall-off region between second order and third order kinetics over the pressure range studied.

The Arrhenius expressions obtained from least squares analyses of the data in Table 1 are given in Table 2. The rate constants reported here may be used to calculate lifetimes due to reaction with OH radicals of ~160 days, ~40 days and ~2 days for CH_3CN, C_2H_5CN and $CH_2=CHCN$, respectively, at 298 K, assuming an atmospheric OH radical concentration of ~1 x 10^6 cm^{-3}. Thus, from these data and the data obtained from the environmental chamber studies, it is obvious that the major atmospheric loss process for these nitriles is reaction with the OH radical, with CH_3CN and C_2H_5CN being less reactive than ethane, but with acrylonitrile reacting at a significant rate under atmospheric conditions.

Effect of NH_3 on NO_x-Air Irradiations. Since low levels of NH_3 are expected to be emitted in the thermal ammonia injection processes, it is of interest to ascertain the effects of this emitted NH_3 on photochemical air pollution. The simplest and most unambiguously interpretable photochemical system is the irradiated NO-NO_2-air system with added propene/propane as a radical trace (see Section IV).

Accordingly, two irradiations were carried out using the SAPRC ~40,000-liter volume outdoor Teflon chamber under dual mode conditions.

Table 1. Rate Constants for the Reactions of OH Radicals with
Acetonitrile, Propionitrile and Acrylonitrile

Reactant	Temperature K	10^{13} k cm^{3}molecule^{-1}sec^{-1}[a]
Acetonitrile	297.2	0.494 ± 0.06
	348.0	0.620 ± 0.07
	423.8	1.05 ± 0.15
Propionitrile	298.2	1.94 ± 0.20
	350.8	2.33 ± 0.25
	384.0	3.62 ± 0.36
	423.0	4.14 ± 0.40
Acrylonitrile	299.0	40.6 ± 4.1
	349.6	40.4 ± 4.1
	422.5	40.2 ± 4.0
	298.7[b]	43.2 ± 4.3
	298.7[c]	48.0 ± 5.0

[a]The indicated error limits are the estimated overal error limits and
include the least square standard deviations as well as the estimated
accuracy limits of flow meter calibrations, pressure measurements, etc.

[b]Total pressure 100 torr argon.

[c]Total pressure 500 torr argon.

Table 2. Arrhenius Parameters for the Reactions of OH Radicals with
Acetonitrile, Propionitrile and Acrylonitrile

Reactant	10^{13} A cm^{3}molecule^{-1}sec^{-1}	E cal mole^{-1}[a]
Acetonitrile	5.86	1500 ± 250
Propionitrile	26.9	1590 ± 350
Acrylonitrile	40.4 ± 0.45[b]	—

[a]The indicated errors for the Arrhenius activation energies are the
estimated overall error limits.

[b]50 torr total pressure argon. No observable temperature dependence.

These irradiations consisted of (a) an NO-NO$_2$-propene-propane-air irradiation with added NH$_3$ in one side of the dual-mode chamber, and (b) an NO-NO$_2$-propene-propane-HNO$_3$-air irradiation with added NH$_3$ (at ~1 ppm concentration) in one side of the dual-mode chamber. In both irradiations, the initial concentrations were: NO ~0.4 ppm; NO$_2$ ~0.1 ppm; and for the added HNO$_3$ irradiation, HNO$_3$ ~0.5 ppm. Table 3 summarizes the hydroxyl radical levels calculated from the propene/propane ratio data.

As seen from Table 3, for the irradiated NO-NO$_2$-air mixture with added NH$_3$ on side A (Run 2), the two sides of the irradiated bag behaved essentially identically, although there was a somewhat higher particulate burden on the added ammonia side, as expected. For the irradiated NO-NO$_2$-HNO$_3$-air system with and without added NH$_3$ (Run 3), the data (Table 3) again show that within the experimental errors the chemistry occurring is identical, as evident, for example, by the identical hydrocarbon decay rates in sides A and B. Furthermore, since side A (with added NH$_3$) had, as expected, substantially higher particulate levels (~50-80 μm^3 cm^{-3} in side A versus 0-2 μm^3 cm^{-3} in side B), it is obvious that the presence of particulates had no effect on the OH radical concentration. As a control experiment, prior to the added NH$_3$ irradiations, an NO-NO$_2$-air irradiation in the entire (undivided) bag (Run 1) was carried out. As seen from Table 3, the radical levels were, within the analytical accuracy, identical to those obtained in the divided bag with and without added NH$_3$.

These data imply that: (a) the addition of NH$_3$ has a negligible effect on radical levels, NO to NO$_2$ conversion, and NO$_x$ loss in irradiated NO$_x$-hydrocarbon-air systems, and (b) the expected increased particulate burden associated with NH$_3$ emissions (due to NH$_3$ + HNO$_3$ → NH$_4^+$NO$_3^-$) also has no observable effect on radical levels, NO to NO$_2$ conversion or NO$_x$ loss.

B. An Experimental Investigation of Offgasing of Nitrogenous Compounds in the SAPRC 5800-Liter Chamber

For the past several years, under funding from the California Air Resources Board and other agencies, we have been studying the effects of a

Table 3. OH Concentration Levels in Outdoor NO_x-Air Irradiations

Run No.	Conditions	OH Concentration, Radical cm^{-3} [a]	
		Side A	Side B
1	Undivided bag NO–NO$_2$–air	0.93 x 10^6	
2	Divided bag NO–NO$_2$–air ~1 ppm NH$_3$ side A	1.1 x 10^6	1.1 x 10^6
3	Divided bag NO–NO$_2$–HNO$_3$–air ~1 ppm NH$_3$ side A	(1.2 ± 0.2) x 10^6	(1.0 ± 0.2) x 10^6

[a]Calculated from the formula

$$[OH] = (k_2-k_1)^{-1}dln([propane]/[propene])/dt$$

where k_1 and k_2 are rate constants for the reaction of OH with propane and propene, respectively (Atkinson et al., 1979).

variety of physical parameters on the formation of simulated photochemical smog. In our previous SAPRC-ARB chamber program (Contract No. A7-175-30), a series of experiments were carried out in the 5800-liter evacuable chamber to determine the effects of temperature on smog formation. These experiments involved irradiations of surrogate hydrocarbon–NO_x–air mixtures and (for control purposes) alkane–NO_x–air mixtures at 282, 303 and 323 K under controlled conditions, including a constant water concentration of 5 x 10^3 ppm. The results of those experiments indicated that radical levels and ozone yields increase significantly as the temperature is increased. Furthermore, for most of the runs carried out at 323 K, the total NO_x consumption rates were considerably less than expected based on the known NO_x removal reactions, and in one experiment the total monitored NO_x levels actually increased. This may in part be due to HNO$_3$ interferences

on the commercial NO-NO$_x$ analyzer employed (Winer et al. 1974, Spicer and Miller 1974, Joseph and Spicer 1978). It is not clear how such observations can be accounted for by homogeneous gas phase chemical processes, and the possibility of their being due entirely to heterogeneous or chamber effects cannot be eliminated.

Clearly, before these and other evacuable chamber irradiations can be reliably used for model validation or for assessing the effects of various parameters on smog formation, the role of chamber effects in influencing such data must be elucidated.

In order to better characterize the role of HNO$_3$ interferences in affecting our NO$_x$ data and in order to determine if HNO$_3$ is involved in the chamber effects, a considerable amount of effort was expended in an attempt to develop a reliable continuous HNO$_3$ analyzer based on modified chemiluminescence NO-NO$_x$ analyzers such as those described by Kelly et al. (1979) and by Joseph and Spicer (1978). The modifications exploited the facts that the molybdenum converters used in such analyzers correct HNO$_3$ to NO (Winer et al. 1974, Joseph and Spicer 1978) and that nylon filters efficiently remove HNO$_3$ (Joseph and Spicer 1978). Several modifications of a commercial TECO 14B/E instrument were carried out with the molybdenum converter being removed from the instrument housing and placed physically as close to the chamber as possible in order to minimize HNO$_3$ losses on sample lines.

The most successful configuration tried is shown in Figure 1. In this configuration, a continuous gas flow through both the unfiltered and filtered converter was achieved by using two solenoids simultaneously switched to select which gas flow goes to the detector and which is discarded. This configuration eliminated the problem with previous configurations caused by HNO$_3$ absorption and desorption, and the readings obtained on the automatic (alternating) mode were found to be consistent with those in the manual modes, with the unfiltered channel giving appropriately higher readings than the filtered channel when HNO$_3$ was present in the gas being sampled. However, it was found that the output of the two converters gave different readings when the gas being sampled contained no HNO$_3$ or when no nylon filters were employed; and when the nylon filter was switched from one converter to the other, different results were obtained.

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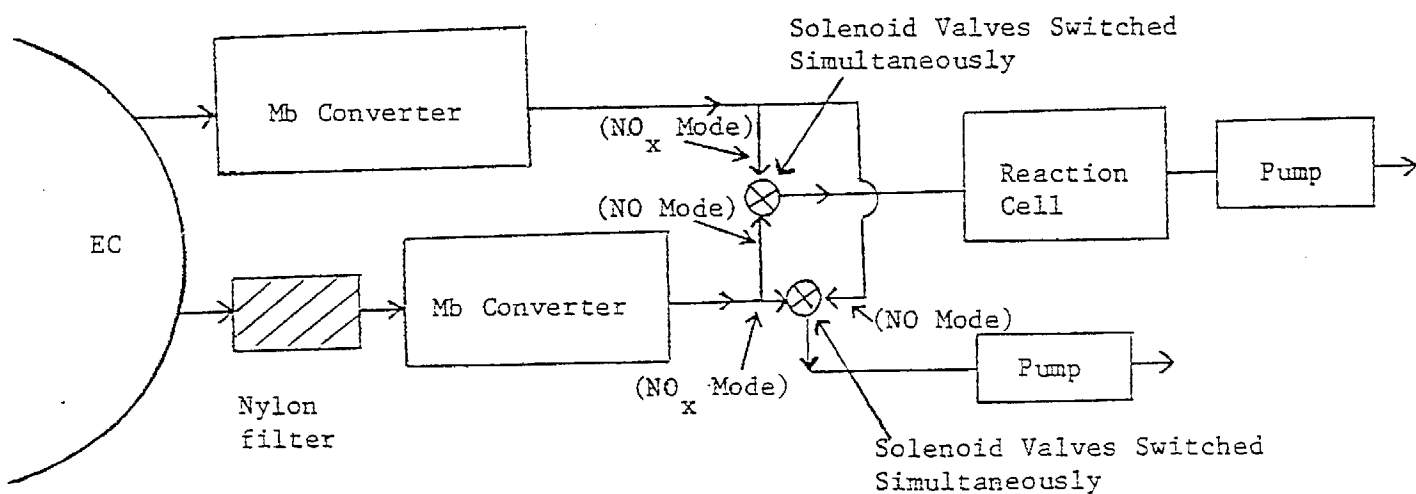
Figure 1. Schematic of configuration used to monitor nitric acid.

These discrepancies generally amounted to 10 to 20% of the total NO_x and appeared to be worse when the gas being sampled was humidified. This problem is probably inherent in the use of molybdenum converters for NO_x monitoring, and all NO_x data obtained using this technique must be considered to be uncertain by at least 10 to 20%.

Two sets of offgassing experiments were then conducted. One set was carried out with the chamber in a relatively contaminated condition following a series of dark experiments which involved injecting O_3 (0.1-1 ppm), NO_2 (5-10 ppm), phenols and other aromatics (~0.1 ppm), and alkenes (~0.1 ppm) in 1 atm air in the chamber. The other set followed an overnight evacuated bakeout ($\leq 10^{-4}$ torr at 366 K) of the chamber. In both sets of experiments, the chamber was filled with pure air at ~5% RH and oxides of nitrogen were monitored using both the modified (see Figure 1) and an unmodified TECO NO-NO_x analyzer. The chamber temperature was held first at ~303 K, then at ~328 K, and finally at ~363 K. At the highest temperature, gas samples were taken for gas chromatographic analysis of organics.

Additional experiments were carried out utilizing the capability of our differential UV-visible spectrometer (DUVVS) interfaced to the chamber to monitor the possible formation of nitrous acid (HONO). This system had a detection limit of ~20 ppb for HONO in the configuration used.

The offgassing rates obtained using the modified and unmodified NO-NO_x instruments are summarized in Table 4 for experiments carried out both before and after the evacuated bakeout. It can be seen that before the evacuated bakeout, NO_x offgassing occurred at 303 K and increased dramatically as the temperature was increased. After the evacuated bakeout, offgassing was still significant at the higher temperatures, but was a factor of ~3 lower than before. At 303 K the NO_x levels actually decreased from the background present in the pure air fill, indicating that NO_x adsorption onto the walls was probably occurring.

Contrary to our initial expectations, offgassing of NO_2 was insignificant even in the contaminated chamber, since the offgassed material consisted primarily of NO and some nitrogenous material which was converted to

Table 4. Offgassing Rates (ppb hr^{-1}) of Nitrogenous Compounds in the SAPRC Evacuable Chamber

| Conditions | Unmodified TECO[a] | | | Modified TECO | |
	NO	NO$_2$	NO$_x$	NO$_x$[a]	NO$_x$ + Nitrate[b]
Before Evacuated Bakeout					
303 K	0.3	0	0.3	0.3	0.8
328 K	2.4	0	2.4	2.4	~10
363 K initial	78	0	78	70	140
final[c]	69	0	69	62	84
After Evacuated Bakeout					
303 K	−0.2	—	—	−0.02	−0.6
328 K	0.7	—	—	—	—
363 K	27	4	31	18	34

[a]Nylon filter in line
[b]No nylon filter; nitrate presumed to be HNO$_3$.
[c]Approximately four hours after 363 K temperature attained.

NO by the molybdenum converter, and which was trapped by nylon. This material is probably primarily HNO$_3$; if HONO was formed, it was at levels less than the ~20 ppb sensitivity of the DUVVS system. HONO was only detected in one experiment in which the chamber was held at ~363 K overnight. In that run, a trace (~20 ppb) of HONO was detected using the DUVVS system.

In order to determine the extent of offgassing of organic materials at high temperatures, samples were taken for gas chromatographic analyses during both of the 363 K temperature offgassing runs. A variety of chromatographic columns, employing both flame ionization and electron capture

detection were used. In both experiments, no significant increase in organic material over the background levels characteristic of our pure air were observed, even when a total carbon analyzer was employed. It is obvious from the results of these experiments that offgassing of nitrogenous species can be significant in the SAPRC evacuable chamber especially at elevated temperatures, and that this offgassing is reduced, but not eliminated, by an evacuated bakeout of the chamber. The major species offgassed appear to be NO and HNO_3, with lesser amounts of NO_2 being observed. The nature and chemical or physical mechanism of this effect is presently unknown, but clearly it must be taken into account in the analysis of data from runs carried out at elevated temperatures in chambers with Teflon coated interiors, and may be important in other types of chambers as well.

C. An Experimental Investigation of Chamber Dependent Radical Sources

An important aspect of the development of reliable computer models for the formation of photochemical smog is their validation against smog chamber data. This requires not only a complete understanding of the kinetics and mechanisms of the chemical reactions which occur during the photooxidations of part-per-million (ppm) concentrations of NO_x and organics in air, but also an adequate and quantitative understanding of major chamber effects.

Recent computer modeling studies have shown that the presence of an as yet unknown source of radicals is necessary in order to match computer-predicted time-concentration profiles with the results of smog chamber experiments (Hendry et al. 1978, Falls and Seinfeld 1978, Carter et al. 1979a, Whitten et al. 1979, 1980; Atkinson et al. 1980).

To date, modelers have differed on how best to represent this radical source in their mechanisms, although it is generally assumed to be chamber dependent. In recent studies, Falls and Seinfeld (1978) and Whitten et al. (1979, 1980) have used only initial nitrous acid (HONO) (presumed to be formed heterogeneously during the injection of NO_x), while Carter et al. (1979a) and Atkinson et al. (1980) have used a constant radical flux, and Hendry et al. (1978) have used a combination of the two. These approaches are significantly different, since the use of initial HONO leads to a

rapidly decreasing radical flux, while a constant radical source results in a considerably greater total radical input during a typical environmental chamber irradiation.

Clearly, aspects of the photochemical mechanisms relating to radical initiation and termination processes cannot be unambiguously validated using smog chamber data until this presently poorly characterized radical source is elucidated. Despite previous studies of "dirty chamber effects" (Wu et al. 1976; Bufalini et al. 1972, 1977), no systematic investigation of chamber-dependent radical sources has been reported to date.

In the present study, a series of NO_x-air irradiations have been carried out under a variety of conditions and in four environmental chambers in order to investigate more directly the characteristics and magnitude of this excess radical initiation effect. Initial NO concentrations ranged from ~0.1 to 1.8 ppm and initial NO_2 from ~0.05 to 0.5 ppm, and in order to monitor hydroxyl radical levels, ~10 ppb each of propene and propane were included in the reaction mixture. Hydroxyl radical levels were determined from the rate of decrease of the propene/propane ratio, based on the assumption that reaction with OH is the only significant loss process for these species (see discussion). Thus,

$$[OH] = (k_2-k_1)^{-1} \, d \ln([propane]/[propene])/dt$$

where k_1 and k_2 are the rate constants for the reaction of OH radicals with propane and propene, respectively. The use of this ratio technique eliminates the necessity to correct for dilution due to sample withdrawal from the chamber and avoids errors due to differences in sample sizes since both species are analyzed on the same gas chromatographic column, as has been discussed previously (Atkinson et al. 1978).

The physical characteristics of the four chambers employed in this study are given in Table 5; the majority of the experiments were carried out in the SAPRC 5800-liter evacuable chamber. A representative set of plots of ln([propane]/[propene]) vs. time, from whose slopes the hydroxyl radical concentrations are derived, are shown in Figures 2. In general, as seen from Figure 2, for runs at $T \leq 303$ K, RH $\leq 50\%$ and $[NO]/[NO_2] > 1$, the OH radical levels remained essentially constant during the two-hour irradiations, while runs where $T \geq 303$ K, RH $> 50\%$ or $[NO]/[NO_2] \leq 1$

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Table 5. Physical Characteristics of the Four Chambers Used

	Evacuable Chamber	Indoor Teflon Chamber	Outdoor Teflon Chamber	Teflon Bag
Location	Indoors	Indoors	Outdoors	Indoors
Volume (liters)	5800	~6000	~40,000	~100
Surface Material	Teflon (TFE)-coated aluminum	FEP Teflon	FEP Teflon	FEP Teflon
Irradiation Source	Xenon arc	Fluorescent blacklights	Sunlight	Fluorescent blacklights
NO_2 Photolysis Rate (k_1)	0.49 min^{-1}	~0.45 min^{-1}	~0.3 min^{-1}	~0.27 min^{-1}
Intensity Profile	Constant	Constant	Diurnal	Constant
NO_x Injection Technique	Vacuum	Syringe	Syringe	Syringe

Figure 2. Plots of ln([propane]/[propene]) against irradiation time for evacuable chamber runs with $[NO_2]$initial $\simeq 0.1$ ppm and varying initial NO concentrations.

generally had initially higher OH radical levels which decreased to a
constant value after ~30 to 60 minutes.

A number of replicate runs were carried out under standard conditions
(NO $\simeq$ 0.4 ppm, NO_2 $\simeq$ 0.1 ppm, ~50% RH (evacuable chamber and indoor Tef-
lon chamber), < 10% RH (small bags), maximum light intensity) in the
various indoor chambers. These duplicate runs gave hydroxyl radical levels
which were reproducible to within $\pm$ 15% in the evacuable chamber, with the
variability in the indoor Teflon chamber and between different small Teflon
bags being somewhat greater. The variability in hydroxyl radical levels in
the large outdoor chamber was considerably greater, with hydroxyl levels
varying by as much as a factor of three, but these can be attributed in
part to variations in temperature and light intensity characteristic of
outdoor irradiations.

A comparison of average hydroxyl radical levels observed in compar-
able runs performed in the four chambers is shown in Table 6. Since the
light intensity of the different chambers is in general different, a more
direct comparison can be obtained from the hydroxyl radical concentration
normalized by dividing by the light intensity (since the OH radical concen-
trations were observed to be proportional to light intensity, as discussed
below). These values are also shown in Table 6. It can be seen that
the intensity-normalized hydroxyl radical levels indeed depend signifi-
cantly on the chamber employed.

The dependence of the OH radical concentration on temperature and
relative humidity for runs in the evacuable chamber, and on humidity for
runs in the indoor Teflon chamber is shown in Table 7 for runs with ap-
proximately the same initial NO and NO_2 concentrations and light inten-
sity. It can be seen that the hydroxyl radical levels increase with both
temperature and humidity. The hydroxyl radical concentrations also appear
to be more strongly affected by humidity in the Teflon chamber than in the
evacuable chamber.

The dependence of hydroxyl radical concentrations on light intensity
is shown in Figure 3, which shows plots of OH radical levels against the
light intensity (as measured by k_1, the NO_2 photolysis rate) for the
5800-liter evacuable and 6000-liter indoor Teflon chamber runs in which the

Table 6. Dependence of OH Radical Levels Observed in Comparable[a]
NO$_x$-Air Irradiations on Chamber Employed

Chamber	k_1[b] (min^{-1})	[OH] (10^6 cm^{-3})	[OH]/k_1 (normalized)[c]
Small Teflon Bag #4	0.27	4.4 ± 0.7	3.1 ± 0.6
Small Teflon Bag #5	0.27	1.4	1.0
Evacuable	0.49	2.5 ± 0.2	1.0
Indoor Teflon	0.45	0.64 ± 0.1	0.3 ± 0.1
Outdoor Teflon	~0.3 ± 0.05[d]	0.9 ± 0.3	0.5 ± 0.2

[a]Initial [NO] = 0.4 ppm; [NO$_2$] = 0.1 ppm; RH < 10%, T = 303–308 K.
[b]k_1 = NO$_2$ photolysis rate.
[c]Normalized to ratio observed in the evacuable chamber runs.
[d]Estimated from radiometer readings using the empirical relationship derived by Zafonte et al. (1977).

Table 7. Dependence of OH Radical Levels Observed in Standard[a]
NO$_x$-Air Irradiations on Temperature and Relative Humidity (RH)

Chamber	T(K)	10^{-6} x [OH] radical cm^{-3}			
		<10% RH	50% RH	80% RH	100% RH
	284	1.6	2.1		4.7
Evacuable	303	2.5	4.4	16 → 11[b]	20 → 12[b]
	323	5.7	18 → 9[b]		50 → 8[b]
Indoor Teflon	303	0.6	1.8		

[a]Initial [NO] ≃ 0.4 ppm; [NO$_2$] ≃ 0.1 ppm; NO$_2$ photolysis rate k_1 = 0.49 min^{-1} (evacuable chamber), 0.45 (indoor Teflon chamber).
[b]OH radical concentrations changed throughout the run; initial and final values given.

Figure 3. Dependence of average OH radical concentrations on the NO$_2$ photolysis rate k$_1$ for irradiations in which the light intensity was varied (O – 5800–liter evacuable chamber; ● – 6000–liter all–Teflon chamber).

light intensity was varied. It can be seen that within experimental error the radical levels are proportional to light intensity.

The effect of NO levels on the results of the evacuable chamber runs is shown in Figure 2, which shows plots of ln([propane]/[propene]) against irradiation time for runs with a similar initial NO_2 concentration, but with initial NO concentrations varying from 0.116 to 0.797 ppm. It can be seen that the final OH radical levels (e.g., the slopes of the lines in Figure 2) are essentially unaffected by the NO concentration, but that the initial slope increases as the NO level is decreased. The hydroxyl radical levels in the evacuable chamber runs were also not strongly affected by NO_2 levels, except in the initial stages of irradiation, where higher NO_2 levels resulted in higher initial hydroxyl levels.

The gas phase chemistry in irradiated NO_x-air systems is well known (Hampson and Garvin 1978, Atkinson et al. 1980, Atkinson and Lloyd 1980), and the presence of trace amounts of propane and propene have a negligible effect on this chemistry (Carter et al. 1979a, Atkinson and Lloyd 1980). The hydroxyl radical levels observed in all the runs reported here were significantly higher than expected from the homogeneous reactions discussed above. This is illustrated in Figures 4 and 5, which show hydroxyl radical concentration-time profiles derived from the data of a representative standard evacuable chamber run, and from a representative high initial NO_2 concentration run and compares them with results of model calculations using only the known gas phase chemistry (Carter et al. 1979a, Atkinson et al. 1980, Atkinson and Lloyd 1980). It can be clearly seen (curve A) that the known radical sources are at least an order of magnitude too low to account for the observed radical levels in these runs.

These figures also show the results of model calculations assuming (B) only initially present HONO (at levels adjusted to fit the initial hydroxyl radical concentrations) and of calculations (C) assuming a constant radical flux at rates adjusted to fit the final OH radical levels, together with calculations (D) assuming a combination of both. It can be seen that assuming only initial HONO greatly underpredicts radical levels after the initial ~15 minutes of the run, and initial HONO can be, at best, only a minor contributor to the observed radical source after the first ~30 minutes of irradiation. On the other hand, using only a constant radical

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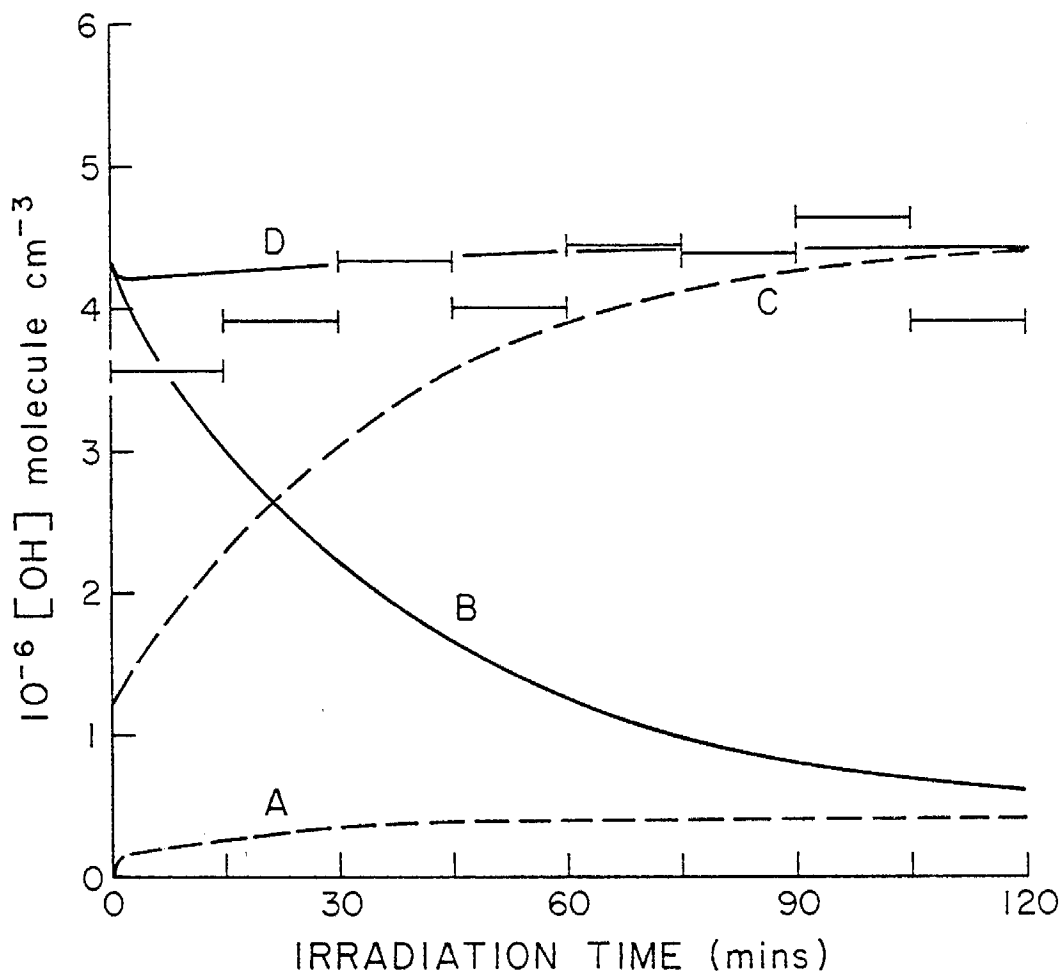
Figure 4. Hydroxyl radical concentrations as a function of
irradiation time. |———| experimental data for EC-
457; [NO]initial = 0.499 ppm, [NO₂]initial = 0.115
ppm; [propane]initial = 0.013 ppm, [propene]initial
= 0.010 ppm; [HCHO]initial ≃ 0.020 ppm, T = 303 K,
RH = 50%, NO₂ photolysis rate constant k₁ = 0.49
min⁻¹; A – model calculations with the homogeneous
gas phase chemistry; B – model calculations with
[HONO]initial = 0.010 ppm; C – model calculations
with a constant OH radical flux of 0.245 ppb min⁻¹;
D – model calculations with [HONO]initial = 0.010
ppm and a constant OH radical flux of 0.245 ppb
min⁻¹.

Figure 5. Hydroxyl radical concentrations as a function of
irradiation time. ├─────┤ experimental data for EC-
442; A – model calculations with the homogeneous gas
phase chemistry; B – model calculations with $[HONO]_{initial}$
= 0.050 ppm; C – model calculations with a constant OH
radical flux of 0.61 ppb min^{-1}; D – model calculations
with $[HONO]_{initial}$ = 0.050 ppm and a constant OH radical
flux of 0.61 ppb min^{-1}.

flux in the calculation results in underprediction of initial OH levels, especially in the high $[NO_2]/[NO]$ runs, and best fits to the data are obtained if some contribution due to initial HONO is assumed. However, in terms of the overall input of radicals during a chamber irradiation (typically $\geq$ 6 hours for smog simulation runs), the constant radical flux is by far the more important factor.

The radical flux required to fit the data for a given run can be estimated without the necessity to carry out detailed model calculations from the fact that radical initiation and radical termination must balance. Since the photolytic half life of HONO in these experiments is $\leq$ 15 minutes, HONO is in photostationary state after the first hour and the radical initiation rates for t > 60 minutes in these photolyses can be estimated from the equation:

$$R_u \ (t \geq 60 \ min) \cong k[OH]_{avg}[NO_2]_{avg}$$

where k is the rate constant for the reaction of OH radicals with NO_2.

Although the hydroxyl radical levels, and thus the radical flux, were observed to be unaffected by NO levels, the radical flux is significantly affected by NO_2 levels, and Figure 6 shows the dependence of the calculated radical flux on second-hour average NO_2 levels for the ~50% RH, 303 K evacuable chamber runs. Also included are the two irradiations carried out at lower light intensity (EC-457 and 458) for which the observed radical fluxes have been corrected to a value of $k_1 = 0.49 \ min^{-1}$. The data are fit by the regression line

$$R_u \ (ppb \ min^{-1}) = k_1[(0.30 \pm 0.06) + (2.9 \pm 0.3)[NO_2]_{avg}]$$

(where the NO_2 concentration is in ppm), as shown in Figure 6. It can be seen that although the radical flux increases with $[NO_2]$, the intercept appears to be significantly greater than zero, suggesting that the radical source may be non-negligible even in the absence of NO_2.

The initial hydroxyl radical levels suggest that HONO may be initially present, in addition to the radical source flux. Table 8 summarizes the initial HONO levels and radical fluxes which are necessary to fit the observed OH radical concentrations for selected evacuable chamber runs. It is clear that additional experiments are required to further characterize

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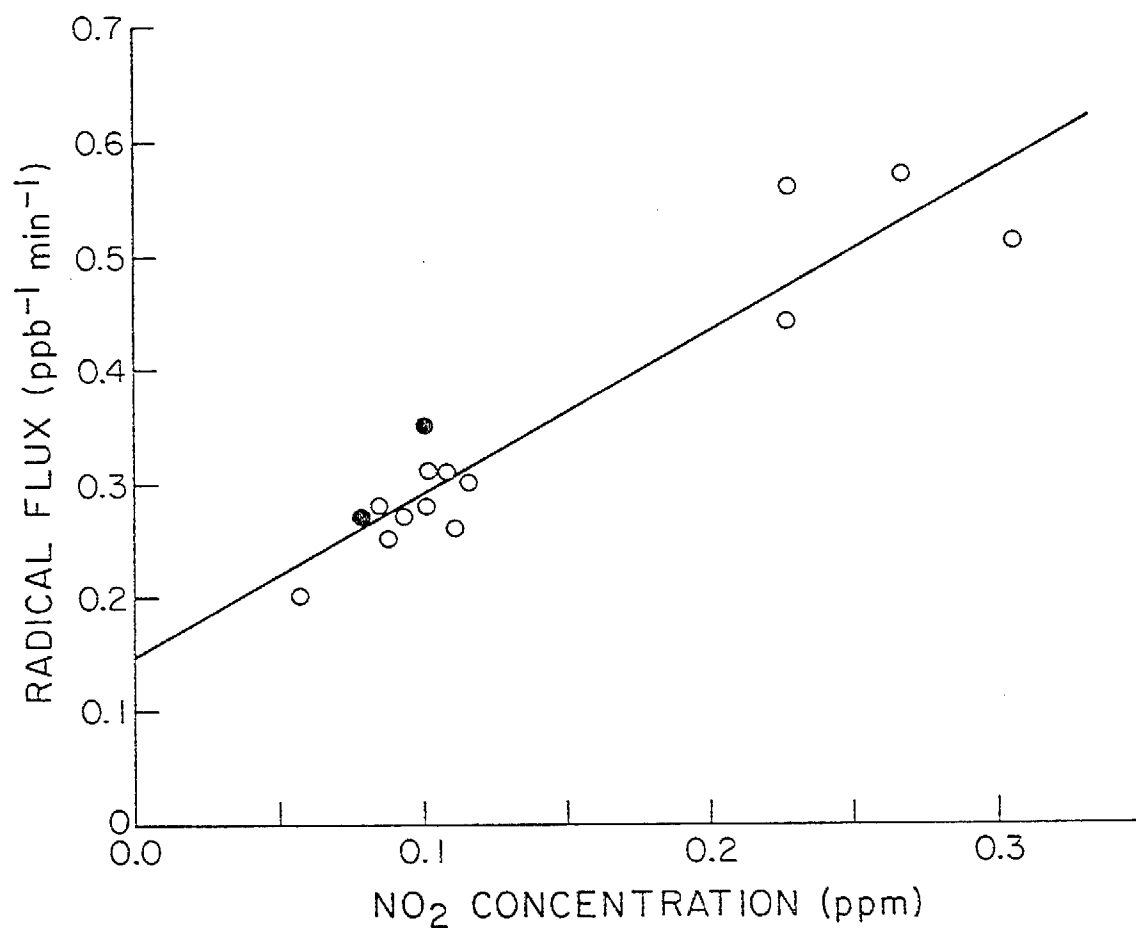
Figure 6. Dependence of estimated radical flux on the average NO_2
concentration for $t > 60$ mins in standard evacuable chamber
irradiations at 303 K and 50% RH. (O – data at $k_1 =$
0.49 min^{-1}; ● – data at $k_1 = 0.25$ min^{-1}, corrected to $k_1 =$
0.49 min^{-1}; see text).

the nature of this radical source and to determine the role, if any, of initially present HONO.

Table 8. Initial Conditions and Empirically Derived Initial HONO and Radical Flux Values for Selected NO_x-Air Irradiations in the SAPRC 5800-Liter Evacuable Chamber

EC Run No.	Temperature K	RH %	Initial NO (ppm)	Initial NO_2 (ppm)	Initial HONO (ppb)	Radical Flux ppb min^{-1}
453	284.5	~0	0.403	0.109	3	0.11
452	284.7	~50	0.375	0.091	4	0.12
454	284.0	~100	0.373	0.081	8	0.25
455	283.4	21	0.120	0.360	16	0.33
443	303.0	~0	0.411	0.099	4	0.17
441	303.4	45	0.431	0.104	7	0.30
457	303.4	~45	0.403	0.093	10	0.27
445	304.2	100	0.411	0.049	15	1.20
437	304.1	42	0.160	0.040	1.5	0.20
464	303.0	~45	0.100	0.093	7	0.25
440	303.0	45	0.674	0.084	3	0.28
442	302.9	52	0.117	0.369	50	0.56
436	302.7	45	1.426	0.364	15	0.51
449	~323.0	~0	0.450	0.110	8	0.40
448	323.4	~50	0.427	0.055	25	1.19
450	324.5	100	0.597	0.140	>100	1.60

D. Exploratory Long-Path FT-IR Studies of the Atmospheric Reactions of
   Model Pesticide Compounds

Increasing attention is being focused on the environmental hazards
posed by pesticide materials and their transformation products in the
entire ecosystem, i.e., in soil, water and the atmosphere. The yearly
application of pesticide chemicals in the United States (Lewis and Lee
1976) presently exceeds one billion pounds and estimates of pesticide
use in California amount to as much as 20% of national use.

Recently, the California Air Resources Board has been concerned
with reactive organic gas emissions from pesticide formulations and their
possible contribution to oxidant formation in the California central
valleys (Weins 1977). Posing the most immediate and serious health hazard,
however, is the exposure of humans to specific active pesticide ingredients
and their possible photodegradation products. Although photodegradation is
an effective pathway for removal of many pesticides in air and other media,
sunlight irradiation has been known to promote "toxic synthesis" leading to
products which are more toxic and potentially more persistent in the
environment than the parent compounds.

It is obvious that knowledge of the phototransformation products of
pesticides in the environment are essential to the safe use of existing
chemicals and the introduction of new ones. While numerous studies on the
photochemistry of various pesticides have been published, the majority of
the experiments have been conducted in aqueous solutions and in other
organic solvents (Rosen 1972, Glofelty 1978). The gas phase photooxidation
studies conducted to date have employed aritifical irradiation and none
have included measures of photochemical reaction rates (Moilanen et al.
1976).

Since the atmosphere is a possible route for significant pesticide
transport and distribution, it is important that studies include not only
the identification of transformation (photooxidation) products but provide
equally important kinetic information on the reactions of pesticidal
materials with the atmospherically important reactive species ozone (O_3)
and hydroxyl (OH) radicals. Such data are essential in providing esti-
mates of atmospheric lifetimes both in the "clean" troposphere and in urban
environments.

The present exploratory work deals with the reactions of O_3 (in the dark) and the OH radical (via photooxidation in the presence of oxides of nitrogen) under simulated atmospheric conditions with three model pesticide compounds: phenyl N-methylcarbamate, trimethylphosphate and trans-1,3-dichloropropene. The first two compounds are representive of carbamates and organophosphates, respectively, classes of compounds which have increasingly replaced organochlorine pesticides. While phenyl N-methylcarbamate [$C_6H_5O\overset{\overset{O}{\|}}{C}NHCH_3$] is not known to be pesticidal, it may be considered structurally as the parent of all ring-substituted carbamates, the majority of which have pesticidal properties. Trimethylphosphate [$(CH_3O)_3P=O$] is the simplest member of the orthophosphate esters and, although not itself used as a pesticide, it is known to be toxic, has mutagenic properties and is of concern as an impurity in commercial organophosphate preparations. The third compound chosen for study was 1,3-dichloropropene (cis and trans isomers) which is used alone as a soil fumigant but is even more widely employed in a 2:1 mixture with 1,2-dichloropropane (known as D-D mixture) for control of nematodes.

Experiments were carried out in a ~30,000-liter FEP Teflon chamber (Figure 7) which contained the multi-pass reflection optics for a long-path Fourier Transform infra-red spectrometer system. A rapid-scan Midac interferometer with a maximum resolution capability of 0.06 cm^{-1} was interfaced to the multiple-reflection optics and was equipped with a dual element, liquid N_2-cooled HgCdTe and InSb detector.

During experiments, NO and NO_2 were monitored by a Bendix chemiluminescence instrument. For some runs, ozone readings were also obtained using a Dasibi UV absorption ozone monitor to supplement those obtained by infrared measurements. The growth and decay of all other species were monitored by FT-IR spectroscopy at pathlengths of 200-540 meters and a spectral resolution of 1 cm^{-1}. At these pathlengths, the strong absorptions of H_2O and CO_2 limit the usable infrared spectral windows to the approximate regions 730-1300, 2000-2300 and 2400-3000 cm^{-1}. Approximately 80 seconds were required to collect the 64 interferograms co-added for each spectrum. Reactant and product analyses were obtained from the intensities of infrared absorption bands by spectral desynthesis (i.e., successive subtraction of overlapping absorptions by known species).
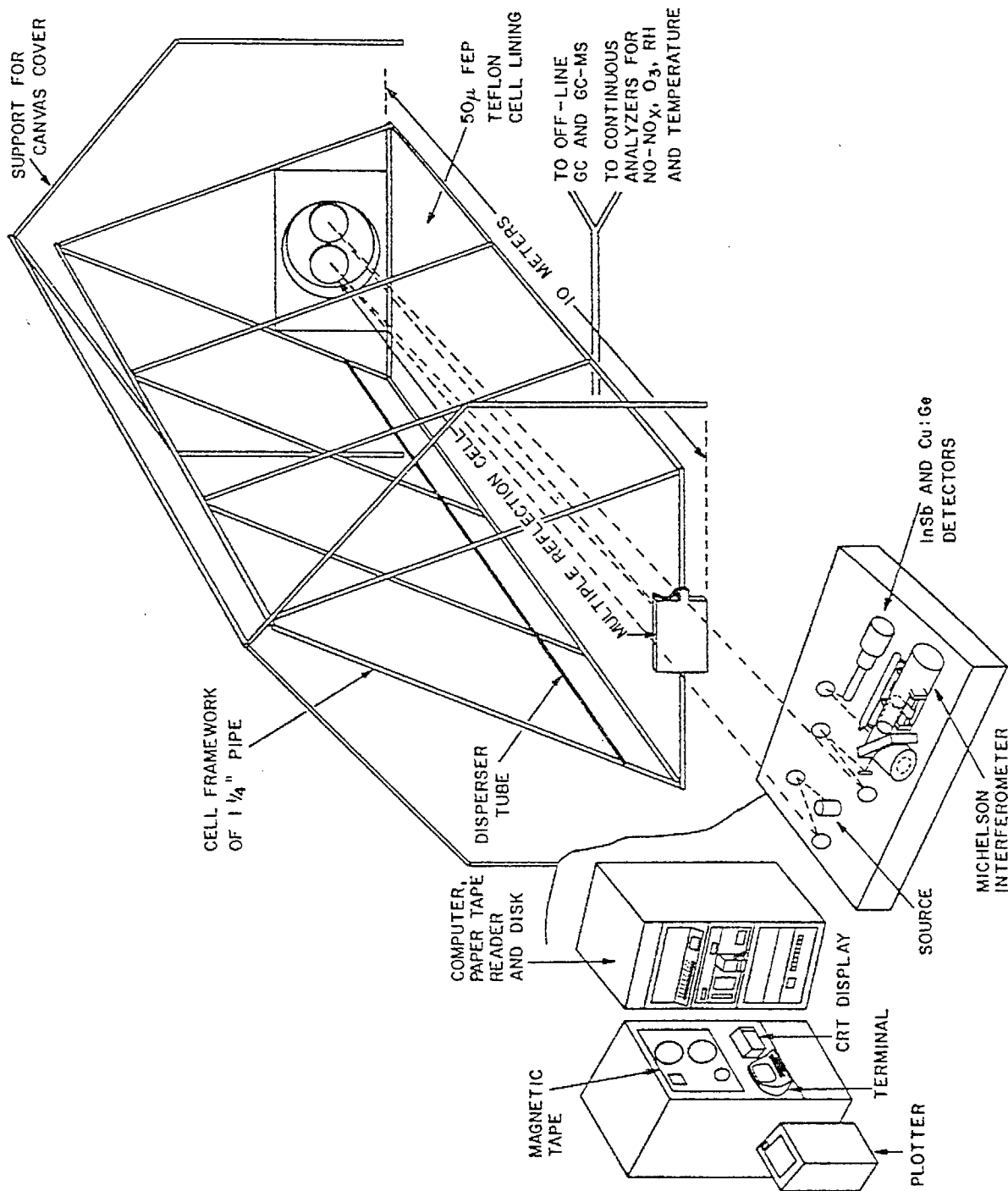
Figure 7. FT-IR spectrometer and 30,000-liter outdoor chamber facility with in-situ multiple reflection optics.

SUPPORT FOR CANVAS COVER

50μ FEP TEFLON CELL LINING

TO OFF-LINE GC AND GC-MS

TO CONTINUOUS ANALYZERS FOR NO-NO$_X$, O$_3$, RH AND TEMPERATURE

10 METERS

MULTIPLE REFLECTION CELL

CELL FRAMEWORK OF 1 1/4" PIPE

DISPERSER TUBE

InSb AND Cu:Ge DETECTORS

MICHELSON INTERFEROMETER

SOURCE

COMPUTER, PAPER TAPE READER AND DISK

MAGNETIC TAPE

CRT DISPLAY

TERMINAL

PLOTTER

For the three model compounds studied, three types of experiments were carried out:

(1) Dark reactions of the compound with O_3

(2) Irradiations of NO_x model-compound air mixtures

(3) Irradiations of NO_x model-compound m-xylene air mixtures.

The latter irradiations were carried out to determine the OH radical rate constants for reaction with the model compounds by monitoring the relative amounts of consumption of the model compound and of m-xylene (Atkinson et al. 1978).

For phenyl N-methylcarbamate and trimethylphosphate, it was observed that although no significant loss of these compounds was observed in experiments of type (a) or (b) at constant temperature, large decreases in concentration were observed when the temperature decreased. These effects are almost certainly due to condensation of these low volatility compounds on the chamber walls, and hence data were only analyzed for constant temperature conditions.

The rate constant data obtained from the matrix of experiments described above are given in Table 9. These rate constant data are in general totally consistent with a-priori expectations from structure-reactivity relationships (Atkinson et al. 1979, Atkinson 1980). From the rate constant data given in Table 9, atmospheric lifetimes can be readily calculated for assumed O_3 and OH radical levels. For atmospheric concentrations of ~0.1 ppm O_3 and 1×10^6 OH radicals cm^{-3}, reaction with the OH radical will dominate for these three compounds, with lifetimes of ~20-50 hours.

Table 9. Summary of Experimental Data for Reactions of Model Pesticide Compounds with O_3 and with the Hydroxyl Radical

Pesticide Compound	Reaction with O_3	Irradiated NO_x-air-compound System	Irradiated NO_x-air -m-xylene-compound System
Phenyl N-methylcarbamate	No observable reaction	No observable reaction	$k^{OH} = 8 \times 10^{-12}$[a]
Trimethylphosphate	No observable reaction	No observable reaction	$k^{OH} \sim 6 \times 10^{-12}$[a]
1,3-dichloropropene	Reaction observed $k = 7.3 \times 10^{-19}$[a]	Reaction observed	$k^{OH} = 1.4 \times 10^{-11}$[a]

[a]Units of cm^3 molecule^{-1} sec^{-1}.

II. INVESTIGATION OF THE ATMOSPHERIC REACTIONS OF NITROGENOUS COMPOUNDS ANTICIPATED FROM NH₃ INJECTION IN ELECTRIC UTILITY POWER PLANTS

The amount of NO and NO_2 formed from the oxidation of the nitrogen in air during the burning of fossil fuels can be significantly reduced by modifications to combustion technology, but such modifications have little effect on the formation of NO_x resulting from the oxidation of fuel-bound nitrogen. On the other hand reduction of NO by ammonia (NH_3) injection has been proposed as a viable method for control of the NO_x formed from both sources in the effluents of fossil fuel burning power plants. At present ammonia appears to be the only compound that is capable of selectively reducing NO_x in the presence of a large amount of oxygen over a wide range of NH_3/NO molar ratios.

Research has been undertaken in both the U.S.A. and Japan to perfect ammonia injection methods employing both catalytic and noncatalytic techniques. Thus, considerable work has been done concerning catalytic enhancement of the rate of the NO_x-NH_3 reaction (Anderson et al. 1962, Nonnenmercher et al. 1966, Griffing et al. 1969, Schmidt et al. 1968) and recent work has concentrated on the development of more active catalysts which are not susceptible to SO_x poisoning (Bauerle et al. 1975a,b; Matsuda et al. 1978, Nobe et al. 1978).

In a parallel program, Exxon Research and Engineering Co. has developed a noncatalytic reduction process which is based on the homogeneous gas phase reaction of NH_3 with NO, which occurs by a complex free radical chain mechanism (Lyon and Longwell 1976, Branch et al. 1979). Discovered by Exxon in 1972, this "Thermal Denox" reaction competes with the oxidation reaction (1).

$$NH_3 + 5/4 \ O_2 \rightarrow NO + 3/2 \ H_2O \tag{1}$$

When ammonia is added to combustion products containing NO at ~1230 K, the NO is reduced to N_2 (Figure 8). However, below 1000 K both the NH_3 and NO pass through the system unaffected, whereas above 1400 K an overall increase in NO occurs. Furthermore, the addition of hydrogen to the system lowers the optimum temperature for NO reduction (Branch et al. 1979).
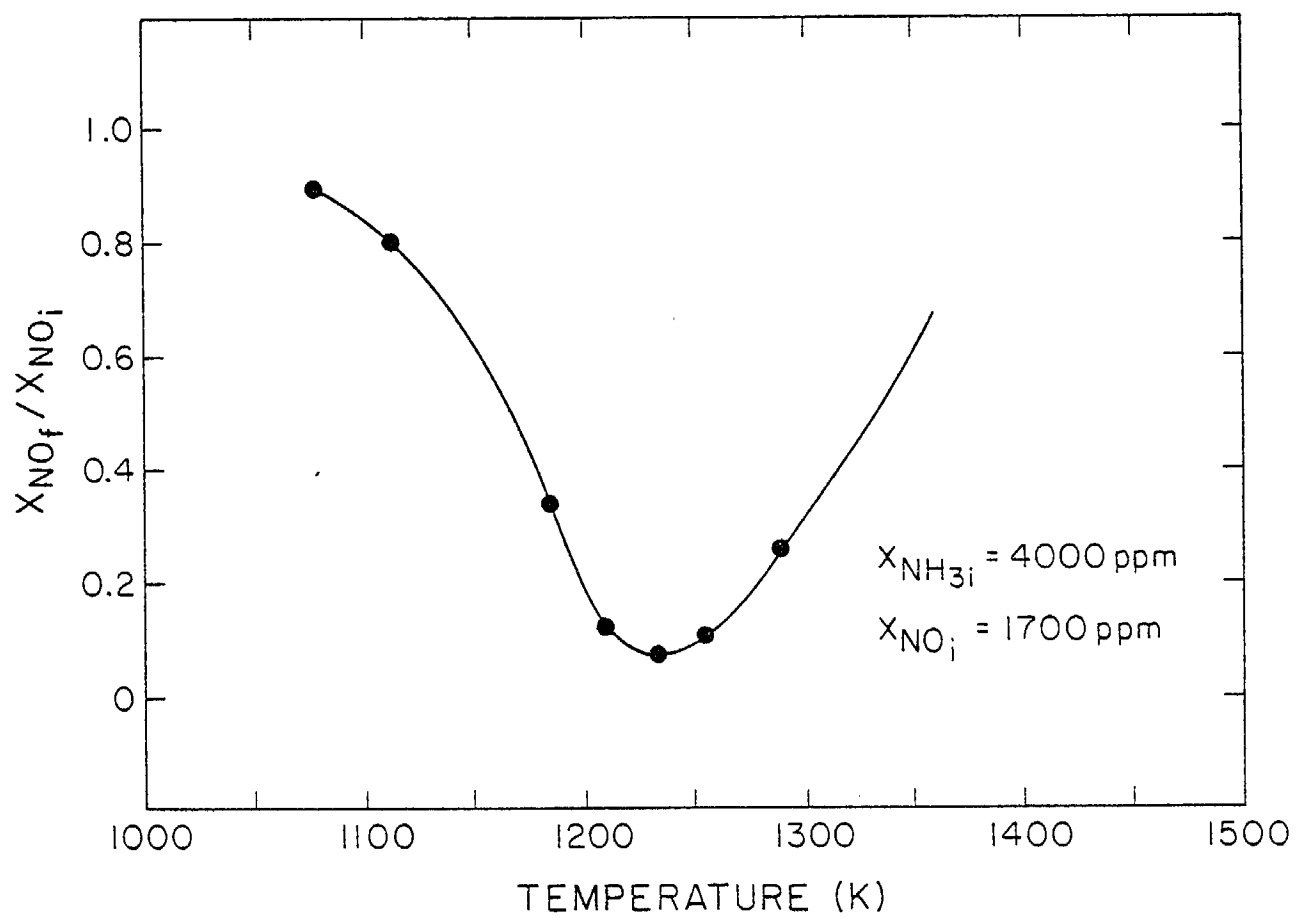
Figure 8. Effect of NH_3 on NO emissions as a function of temperature. From Branch et al. (1979).

Exxon has carried out a commercial demonstration of their patented Thermal Denox process at the Kawasacki refinery of Exxon's Japanese affiliate. Up to a 70% reduction in NO was achieved with this retrofit installation, and Exxon has estimated that this process could be fitted to existing boilers and furnaces in areas with strict NO_x emission standards at a cost of 7 to 15 cents/10^6 BTU.

Pending regulations in California call for approximately 95% reduction in NO_x emissions from sources such as electric utility power plants by 1985. Under the impetus of this requirement serious consideration is being given to application of the Thermal Denox process to power plants in the South Coast Air Basin, and perhaps elsewhere in the state. In view of this, it is important to establish now whether or not significant emissions of NH_3 may occur, and whether, as a result of the complex free radical reactions involved in this process, other compounds may be formed which in themselves may constitute a hazard or which under atmospheric transformations may lead to the formation of toxic species.

In preliminary laboratory studies Exxon workers have identified only five species as pollutant by-products from the Thermal Denox process: N_2O, CO, HCN, SO_3 and NH_4HSO_4. In addition they found that ammonia itself will be emitted at a concentration of at least 5 ppm. However, consideration of actual power plant operating conditions of temperature and oxygen concentration together with available kinetic and thermodynamic data suggested the possibility (Brown 1979) that a number of low molecular weight nitrogenous compounds including alkyl amines and nitriles might be formed at significant concentration levels.

An indication of possible products formed under such conditions can be found in published studies of the ammoxidation (reaction with NH_3 in the presence of O_2) of unsaturated hydrocarbons over metal oxide catalysts at elevated temperatures. Thus, propene yielded acrylonitrile and acetonitrile (Sasaki et al. 1977) and isobutene gave methacrylonitrile and acetonitrile (Rusu et al. 1974)
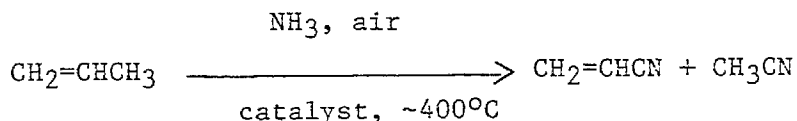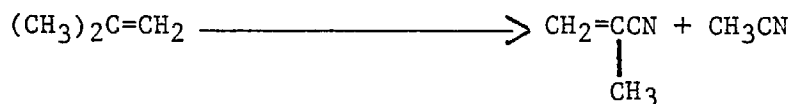
$$CH_2=CHCH_3 \xrightarrow[\text{catalyst, } \sim 400^\circ C]{\text{NH}_3, \text{ air}} CH_2=CHCN + CH_3CN$$

$$(CH_3)_2C=CH_2 \xrightarrow{\hspace{4cm}} CH_2=\underset{\underset{CH_3}{|}}{C}CN + CH_3CN$$

The California Air Resources Board funded a program in the laboratories of Professor Robert Sawyer at the Department of Mechanical Engineering, University of California, Berkeley, to attempt to detect the formation of nitrogenous compounds under laboratory conditions. While our intention was to use the data from this UC Berkeley study to determine which nitrogenous species to study at SAPRC, it was not possible to postpone this phase of the SAPRC study until the Berkeley data became available. Hence, it was decided to investigate the atmospheric reactions of the selected aliphatic nitriles, acetonitrile (CH_3CN), propionitrile (C_2H_5CN) and acrylonitrile ($CH_2=CHCN$). These studies were carried out in two parts: (a) environmental chamber studies of the reactions of these compounds with ozone, the nitrate radical (NO_3) and in irradiated NO_x-air systems, and (b) the determination, using a flash photolysis-resonance fluorescence technique, of the absolute rate constants for the reaction of OH radicals with these selected nitriles. In addition, we have investigated, using an outdoor chamber in dual-mode, the effect of NH_3 on radical levels from NO_x-air irradiations in order to assess the impact of NH_3 emissions on photo-chemical air pollution systems.

A. Environmental Chamber Studies

Studies were carried out to ascertain the major fates of the nitriles CH_3CN and C_2H_5CN under simulated atmospheric conditions.

Experimental. These studies were carried out in the SAPRC ~6400-liter (226 ft^3) all-glass (Pyrex) chamber (Figure 9) which has a surface-to-volume ratio of 3.4 m^{-1} (1.04 ft^{-1}). Photolyzing radiation is provided by two externally mounted, diametrically opposed banks of 40 Sylvania 40-W BL (blacklight) lamps, which are backed by an array of Alzak-coated reflections. The supporting analytical facilities employed in the glass chamber studies are shown in Figure 10, and the analytical facilities employed in these experiments are described in detail below.

Ozone (O_3) was monitored by ultraviolet absorption analyzers (Dasibi Model 1003). These instruments are calibrated using the UV absorption method adopted by the ARB in June 1973.
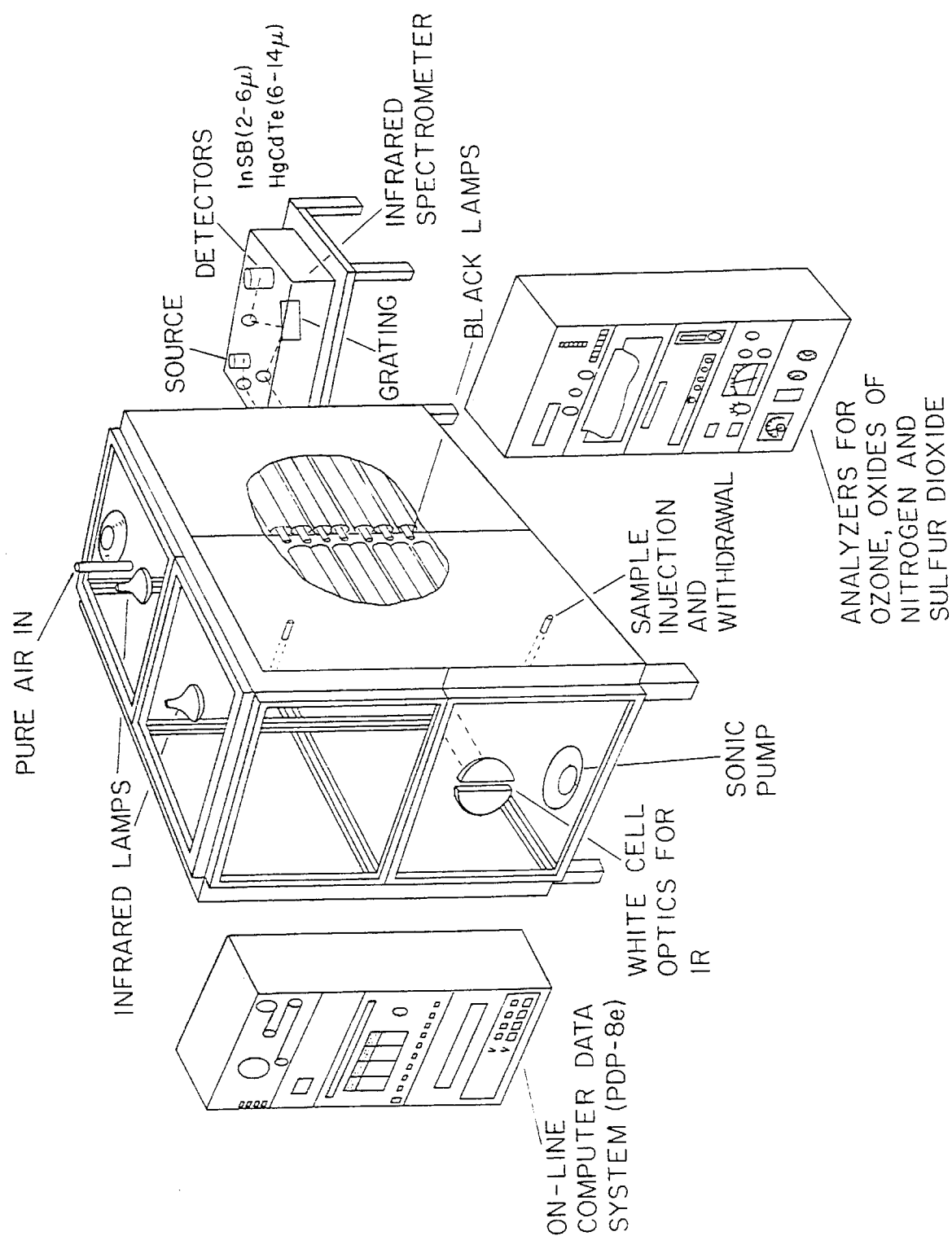
Figure 9. SAPRC 6400-liter all-glass environmental chamber.

PURE AIR IN

INFRARED LAMPS

SOURCE

DETECTORS

InSB(2-6μ)
HgCdTe(6-14μ)

INFRARED
SPECTROMETER

GRATING

BLACK LAMPS

SAMPLE
INJECTION
AND
WITHDRAWAL

ANALYZERS FOR
OZONE, OXIDES OF
NITROGEN AND
SULFUR DIOXIDE

WHITE CELL
OPTICS FOR
IR

SONIC
PUMP

ON-LINE
COMPUTER DATA
SYSTEM (PDP-8e)
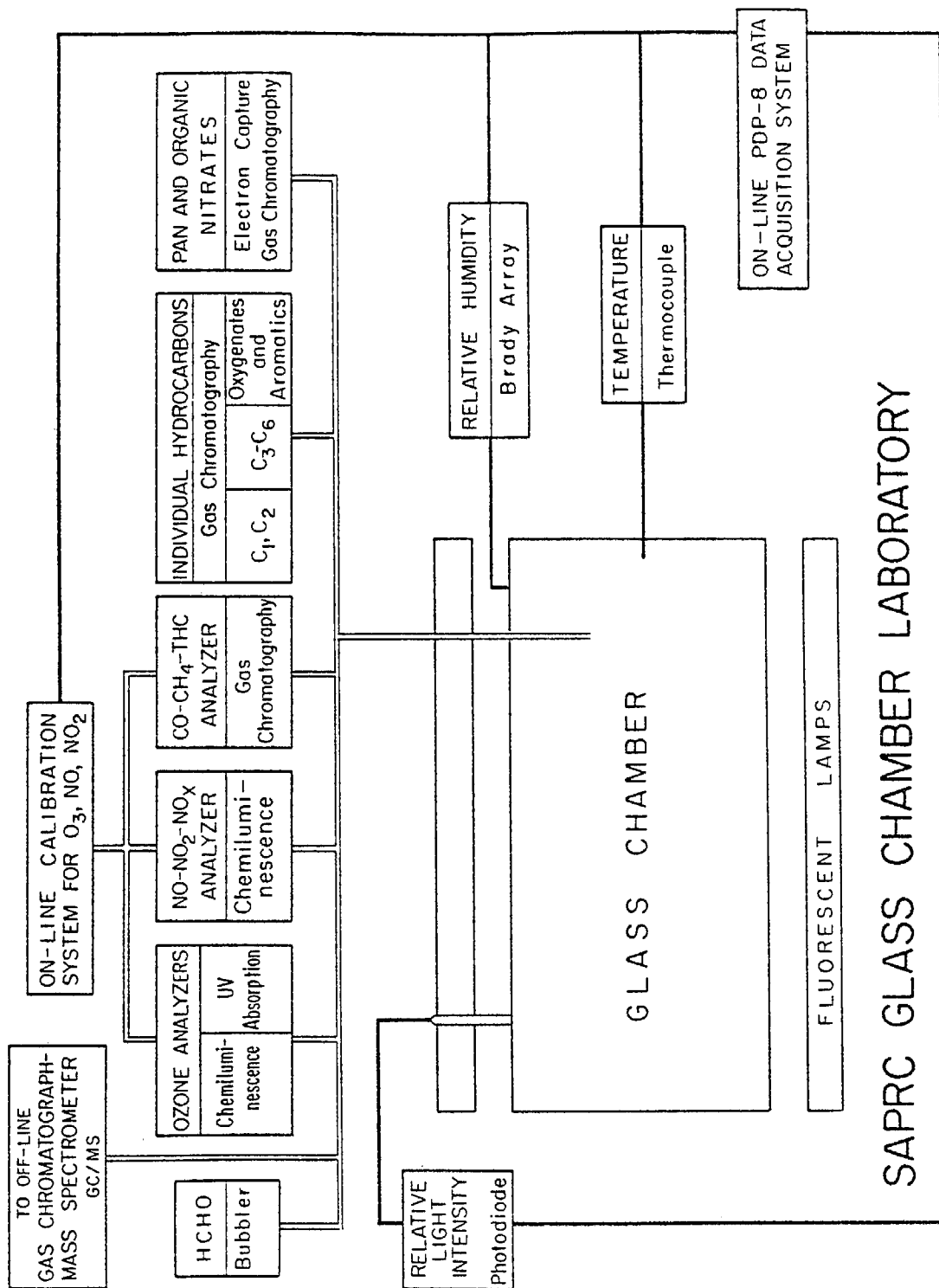
Figure 10. Schematic of all-glass chamber facility.

Nitrogen oxides (NO, NO_2 and NO_x) were monitored by chemiluminescence detection (TECO 14B). The NO_2 and NO_x modes of this and similar chemiluminescence $NO-NO_x$ analyzers have been shown to respond quantitatively to other nitrogen-containing compounds, such as peroxyacetyl nitrate (PAN) and organic nitrates and nitrites (Winer et al. 1974, Spicer and Miller 1974) However, the nitriles used in these studies did not yield any observable response on these $NO-NO_2-NO_x$ instruments.

Sample temperature was read from either a Doric Thermocouple indicator (^{o}F), using a thermocouple suspended in the chamber, or from a $19^{o}C$ to $35^{o}C$ ($0.01^{o}C$/division) thermometer hung free inside the chamber close to the end window, but not in the direct light path.

Relative humidity (RH) was measured using a Brady array (Thunder Scientific). The response in volts (V) was converted to percent RH, using the calibration function supplied by the manufacturer.

Hydrocarbons (HC) were monitored by gas chromatography with flame ionization detection (GC-FID), using the columns and methods developed by Stephens (Stephens and Burleson 1969, Stephens 1973). Methane and C_2 hydrocarbons were analyzed using a 5 ft Poropak N Column, C_3-C_6 HC's using a 36 ft 2,4-dimethyl sulfolane column, and aromatics and oxygenates using a special three-part column. Oxygenates were also monitored using a 10 ft Carbowax 600 column. The chromatographic technique for the analysis of the nitriles is discussed below. Each GC was calibrated frequently using specially prepared samples (Stephens and Burleson 1969). Computer processing of the data includes calculation of the concentration in ppbC for each data point. The data obtained have not been corrected for losses due to sampling from the chamber.

Experimental Procedures. Following each experiment in this program, the glass chamber was flushed with dry air provided by the SAPRC air purification system (Doyle et al. 1977) for about two hours at a flow of ~12 cfm. The chamber was then flushed with humidified pure air for about one hour just prior to the start of a run to achieve the desired initial RH. The temperature of the chamber prior to turning on the lamps was adjusted to the operating temperature anticipated during the irradiation by means of infrared lamps. During all flushing procedures, the two sonic pumps were in operation to provide maximum release of materials from the chamber walls.

The matrix air used during the flushing procedure and for the final fill for the experiment generally contained less than a total 60 ppbC of all hydrocarbons except methane, which was typically at a concentration between 550-850 ppb (Doyle et al. 1977). After completion of filling, analysis of the matrix air prior to injections showed somewhat higher hydrocarbon values due to off-gassing from the chamber walls, but generally these values were less than 200 ppbC nonmethane hydrocarbon.

Following flushing, starting materials were injected using 100-ml precision bore syringes or micropipettes or by flushing the contents of a bulb containing the desired amount of the nitrile into the chamber by a stream of N_2 and rapid mixing was obtained by brief (~5 minutes) use of the sonic pumps. During the run, the sample temperature was controlled at 305 ± 2 K by means of a variable air flow past the chamber walls.

Development of Gas Chromatographic Techniques for the Analysis of the Nitriles CH_3CN and C_2H_5CN. The chromatographic analysis technique previously employed in these laboratories for the studies of the atmospheric chemistry of higher molecular weight amines and alcohol amines was based on Tenax trapping (Pitts et al. 1978). This is not suitable for the low molecular weight nitriles and amines because of their low breakthrough volumes on Tenax (Brown and Purnell 1979). On the other hand, the chromatographic system used for the simple oxygenate analysis, employing cryogenic trapping to concentrate the sample, and columns packed with 5 to 10% Carbowax-600 (C-600) on Firebrick, was also not satisfactory, since unacceptably broad and assymetrical peaks were obtained when the nitriles were injected.

An attempt was made to correct this problem with the C-600 gas chromatographic system by employing an all-glass column and glass-lined metal tubes in the sample concentration trap and injection system, but unsatisfactory peak shapes occurred. Finally, we used the column previously employed on the alcohol amines analysis (10 ft x 2 mm ID glass column packed with 4% Carbowax of 20-M/0.8% KOH on Carbopack B), but with the glass-lined sample-concentration trap and injection system developed for the C-600 system. This column gave excellent peak shapes and separation for the nitriles, and was consequently used for the studies of these compounds.

Results. Experiments were carried out in the ~6400-liter chamber to determine the dark decay rates of acetonitrile and propionitrile in pure air in the presence and absence of O_3 and NO_x. These consisted of the following: (1) injection of ~100 ppb of each nitrile into an atmosphere of pure air, and monitoring its decay; (2) injection of 1.5 ppm of O_3 into the chamber where ~100 ppb of each nitrile has already been injected; and (3) injection of ~0.5 ppm of NO_2 into the chamber containing ~100 ppb of each nitrile and ~1.5 ppm of O_3.

The purpose of the third experiment was to determine if the nitriles react with the nitrate (NO_3) radical which is formed from the reaction of O_3 with NO_2. This possibility had to be examined because we have previously shown (Carter et al. 1981) that reaction with the NO_3 radical is a significant atmospheric degradation pathway of phenolic compounds.

Figure 11 shows the concentrations of the two nitriles, as measured by gas chromatography, as a function of time in the environmental chamber. After the injection of ~1.5 ppm O_3 (at 2.1 hours), the ozone concentrations were continuously monitored with a Dasibi Model 1003 instrument which sampled at a rate of 0.60 liter min^{-1}. Hence from 2.1 hours onward, the calculated dilution rate due solely to sampling was 0.0056 hr^{-1}. However, transfer of air due to ambient temperature and pressure variations also causes dilution of the contents of the chamber, so this calculated dilution rate must be considered a lower limit.

Least squares analysis of the data shown in Figure 11 yields the following loss rates of the two nitriles for the time period $\geq$ 2.1 hours:

$$CH_3CN: -dln[CH_3CN]/dt = 0.00915 \pm 0.00614 \; hr^{-1}$$

and

$$C_2H_5CN: -dln[C_2H_5CN]/dt = 0.00627 \pm 0.00469 \; hr^{-1}$$

where the indicated errors are the single standard derivations. These loss rates in the presence of ~1.5 ppm O_3 or of ~0.5 ppm NO_3 are, within the experimental uncertainties, identical to the expected dilution rate due to sampling and chamber-to-room gas transfer.

No significant decay of either nitrile, other than that which can be attributed to dilution due to sampling or chamber leakage, was thus observed under any of the conditions employed. Thus, removal of these simple
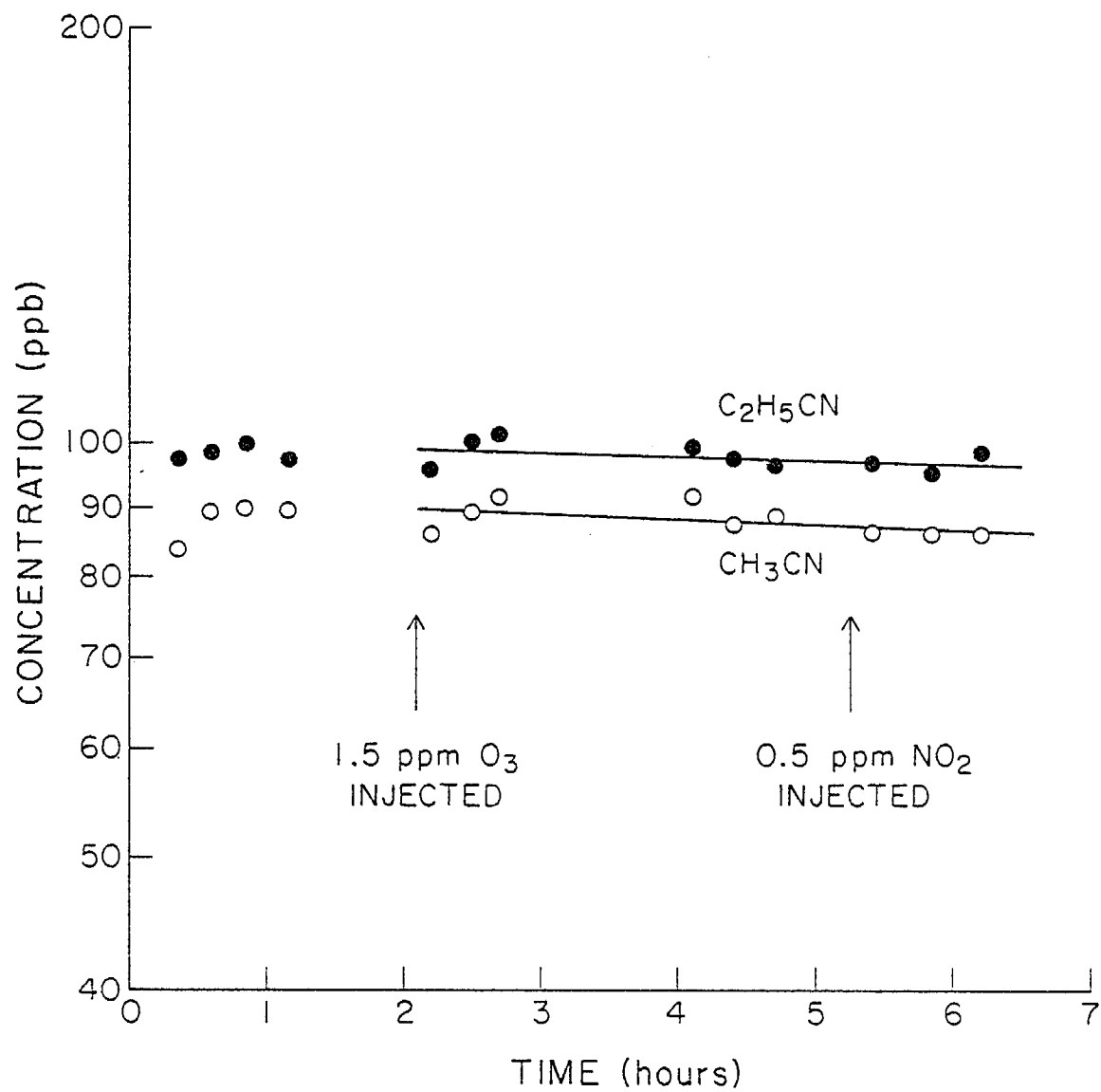
Figure 11. Dark decays of CH_3CN and C_2H_5CN in pure air, in the presence of O_3, and in the presence of $O_3 + NO_2$.

nitriles (CH_3CN and C_2H_5CN) by surface absorption, by reaction with O_3, or by reaction with NO_3, the radical will be negligible under atmospheric conditions.

From these observed nitrile loss rates in the 6400-liter environmental chamber, upper limits to their rate constants for reaction with O_3 can readily be calculated (using a maximum loss rate of the least squares loss rate plus two standard deviations, and allowing for losses due to sampling [$0.0056 \ hr^{-1}$]):

$$O_3 + CH_3CN; \quad k \leq 1.5 \ x \ 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$$

and

$$O_3 + C_2H_5CN; \quad k \leq 1.0 \ x \ 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$$
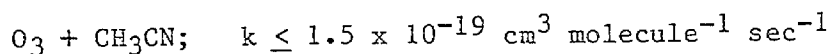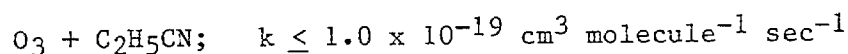
at 299 ± 1 K.

For acrylonitrile ($CH_2=CHCN$), an upper limit to the ozone reaction rate constant has recently been determined (Atkinson et al. 1981) from the decay of O_3 in the presence and absence of $CH_2=CHCN$ to be $k \leq 1.0 \ x \ 10^{-19} \ cm^3 \ molecule^{-1} \ sec^{-1}$ at 296 ± 2 K.

In order to determine the loss rates of the nitriles due to photolysis ~200 ppb of CH_3CN and ~100 ppb of C_2H_5CN were irradiated in pure dry air with ~20-25 ppb of neopentane and n-butane added as tracers to monitor chamber OH radical levels.

The data are shown graphically in Figure 12 as plots of the nitrile concentrations against irradiation time, and as $\ln([neopentane]/[n-butane])$ versus irradiation time. Upon irradiation, both the nitriles and the two alkane tracers were observed to disappear at rates somewhat higher than anticipated from the sampling rates.

From least squares analysis of the data the disappearance rates obtained are:

$$-d\ln[neopentane]/dt = (1.21 \pm 0.02) \ x \ 10^{-3} \ min^{-1}$$
$$-d\ln[n-butane]/dt \ \ = (2.19 \pm 0.04) \ x \ 10^{-3} \ min^{-1}$$
$$-d\ln[CH_3CN]/dt \ \ \ \ \ = (1.09 \pm 0.09) \ x \ 10^{-3} \ min^{-1}$$
$$-d\ln[C_2H_5CN]/dt \ \ \ = (0.88 \pm 0.06) \ x \ 10^{-3} \ min^{-1}$$

The differing disappearance rates of neopentane and n-butane implies the presence of OH radicals from the chamber radical source (see Section IV

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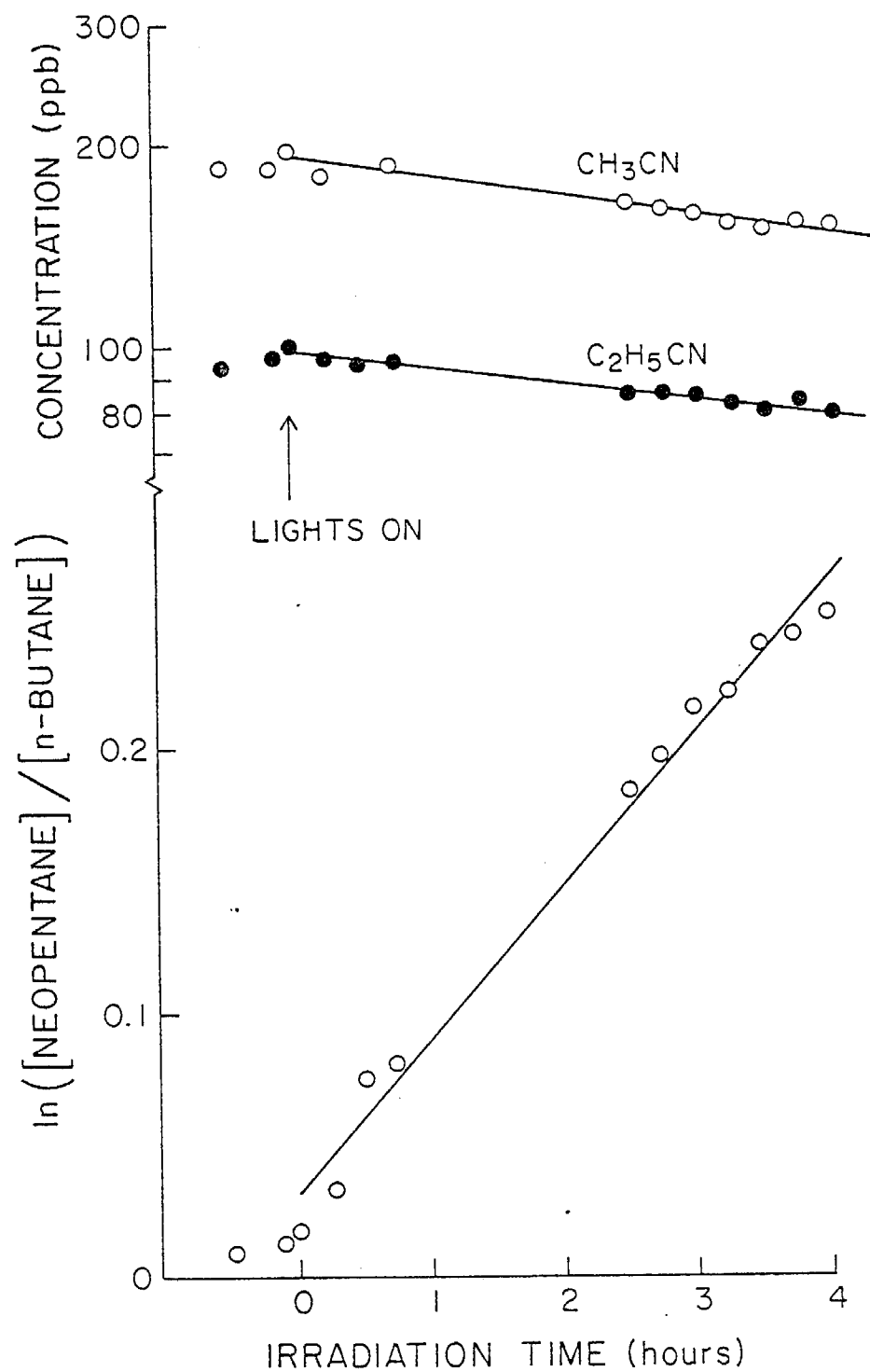
Figure 12. Data from the irradiation of a $CH_3CN-C_2H_5CN$-air mixture containing trace levels of n-butane and neopentane.

for a detailed discussion of these chamber radical sources). The OH radical concentration is most accurately determined from analysis of the neopentane/n-butane concentration ratio data (Atkinson et al. 1978), since this procedure eliminates gas chromatographic sample size differences. From least squares analysis of the ln([neopentane]/[n-butane]) versus irradiation time data (Figure 12), and using [k(OH + n-butane)-k(OH + neopentane) = 1.88 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson et al. 1978), the derived OH radical concentration during the irradiation is [OH] = (8.6 $\pm$ 0.4) x 10^6 cm^{-3}. With this radical level the disappearance rates of neopentane and n-butane due solely to reaction with OH radicals are then calculated to be 0.44 x 10^{-3} and 1.39 x 10^{-3} min^{-1}, respectively. Comparison of these calculated OH radical reaction disappearance rates with the observed values leads to estimated loss rates due to sampling and chamber air exchange with room air of 7.7 x 10^{-4} and 8.0 x 10^{-4} min^{-1}, from the neopentane and n-butane data, respectively. Since these are in excellent agreement, it appears that the chamber dilution rate was 8 x 10^{-4} min^{-1}.

This estimated dilution rate of 8 x 10^{-4} min^{-1} is very similar to the observed nitrile disappearance rates of 1.09 x 10^{-3} (CH_3CN) and 8.8 x 10^{-4} (C_2H_5CN) min^{-1}, showing that photolysis and OH radical radical reactions are essentially negligible under these conditions.

To further investigate the atmospheric reactions of the two nitriles CH_3CN and C_2H_5CN, an irradiation of a NO_x ($NO_{initial}$ = 0.25 ppm, NO_2 initial = 0.10 ppm)-nitrile (~2.0 ppm each)-air mixture, with neopentane and n-butane again added (at ~90-100 ppb) as OH radical tracers, was carried out.

The data are shown in Figure 13, plotted as in Figure 12, and from least squares analyses, the disappearance rates during the irradiation were:

$$-d\ln[\text{neopentane}]/dt = (9.0 \pm 0.3) \times 10^{-4} \text{ min}^{-1}$$
$$-d\ln[\text{n-butane}]/dt = (1.16 \pm 0.04) \times 10^{-3} \text{ min}^{-1}$$
$$-d\ln[CH_3CN]/dt = (4.8 \pm 1.4) \times 10^{-4} \text{ min}^{-1}$$
$$-d\ln[C_2H_5CN]/dt = (4.9 \pm 0.6) \times 10^{-4} \text{ min}^{-1}$$

By an analysis analogous to that for the data shown previously in Figure 12, the OH radical concentration during the irradiation was 2.5 x 10^6 cm^{-3}.
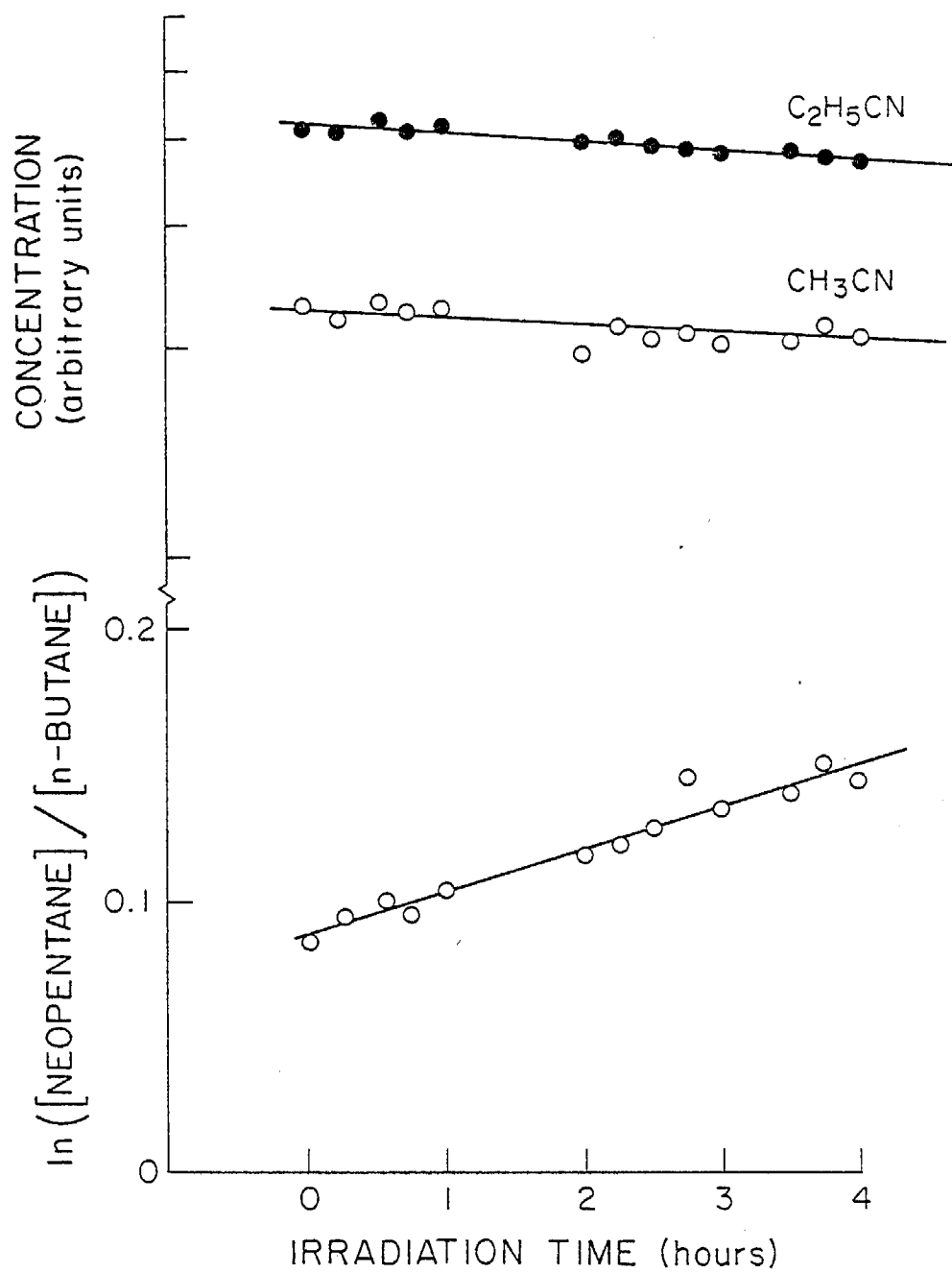
Figure 13. Data from the irradiation of a $CH_3CN-C_2H_5CN-NO_x$-air
mixture with added n-butane and neopentane tracers.

This OH radical concentration leads to disappearance rates due to OH radical reaction of 1.3×10^{-4} and 4.1×10^{-4} min^{-1} for neopentane and n-butane, respectively. This yields, by comparison with the observed disappearance rates, a dilution rate of 7.7×10^{-4} min^{-1} and 7.5×10^{-4} min^{-1} from the neopentane and n-butane data, respectively.

The two nitriles were observed to have disappearance rates less than this estimated dilution rate, and hence no evidence of photolytic or chemical reaction loss rates could be obtained, in agreement with the nitrile-pure air photolysis.

To obtain further quantitative information concerning OH radical reaction rate constants, absolute rate constants were determined using the flash photolysis-resonance fluorescence technique available at SAPRC, as described below.

B. Determination of Absolute Rate Constants for the Reaction of OH Radicals with Nitriles

Experimental. The apparatus and techniques used have been described previously (Harris et al. 1980), hence only a brief description will be given here. Hydroxyl radicals are produced by the pulsed vacuum ultraviolet photolysis of H_2O at wavelengths $\lambda \geq 115$ nm (MgF_2 cut-off) and their concentration monitored as a function of time after the flash by resonance fluorescence. The reaction vessel is a Pyrex cylinder, 20 cm in length and 12 cm in diameter, fitted with two quartz windows at right angles to one another. The flash lamp is operated at discharge energies of 30-120 joules per flash and repetition times of one flash every three seconds.

The OH resonance radiation is produced by a 2450 MHz microwave discharge through a flow of 3% H_2O in argon at ~1 torr total pressure. The radiation from the resonance lamp is focused into the reaction vessel at right angles to the flash beam. Resonance fluorescence from the hydroxyl radicals is observed at right angles to both the flash beam and the resonance radiation by a cooled EMI 9659QA photomultiplier tube fitted with an interference filter with a center wavelength of 308.9 nm and a half-band bandwidth of 2.0 nm. This interference filter transmits mainly the 306.4 nm band of $OH(A^2\Sigma^+, v' = 0 \rightarrow X^2\Pi, v'' = 0)$. The intersection of the aperture of the detection system and the resonance radiation beam defines a

fluorescence viewing zone of approximately 2 cm cross section at the center of the reaction vessel. This region is well separated from the walls, thus minimizing wall losses of OH radicals. Signals are obtained by photon counting in conjunction with a Nuclear Data ND-2400 multichannel analyzer operated in the multichannel scaling mode.

The reaction cell is enclosed in a furnace, the temperature of which can be held constant to better than ± 1 K over the temperature range 295-475 K, and the gas temperature is measured by a Chromel/Alumel thermocouple mounted inside the reaction vessel but clear of the fluorescence viewing zone.

All experiments are carried out under flow conditions so that the gas mixture in the reaction vessel is replenished every few flashes to avoid the accumulation of photolysis or reaction products and to minimize problems associated with adsorption of the reactants on the reaction vessel walls. The partial pressure of H_2O in the reaction cell typically ranged from 0.01 to 0.03 torr. Reactant concentrations were controlled by saturating a known fraction of the argon diluent gas flow with the nitrile at 298 K (CH_3CN and C_2H_5CN) or at 228 K ($CH_2=CHCN$). The nitrile partial pressures in this fraction of the argon flow were measured by spectrophotometry in the IR or UV (CH_3CN: CN stretch at 2280 cm^{-1}, CH_3CH_2CN: CH stretch at 3010 cm^{-1}, both using a Perkin-Elmer 283 IR spectrometer; $CH_2=CHCN$ at 207 nm using a Cary 15 UV-visible spectrophotometer). The systems were calibrated by measuring the optical absorption of known pressures of the nitriles as determined by an MKS Baratron capacitance manometer. All gas flows were monitored with calibrated flow meters and the gases were premixed and thermally equilibrated before entering the reaction vessel.

Results. The reactions of OH radicals with acetonitrile, propionitrile and acrylonitrile were studied over the temperature range 298 to 424 K, typically at a total pressure of 50 torr argon. Under the experimental conditions employed the pseudo-first order decays of the OH radical concentrations following production in the flash are given by the integrated rate expression

$$\frac{[OH]_o}{[OH]_t} = \frac{S_o}{S_t} = \exp[(k_o + k[nitrile])(t-t_o)]$$

where $[OH]_o$ and $[OH]_t$, S_o and S_t are the OH concentrations and resonance fluorescence signal intensities at times t_o and t, respectively; k_o is the first order removal rate constant for OH radicals in the absence of added reactant (attributed primarily to diffusion of OH out of the viewing zone and to reaction with impurities) and k is the rate constant for the reaction

OH + nitrile → products
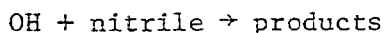
In all experiments, exponential decays of the resonance fluorescence signal were observed and the measured pseudo-first order decay rates were were found to depend linearly on the nitrile concentration.

Figures 14 to 16 show plots of the OH radical decay rate against reactant concentration for CH_3CN, C_2H_5CN and $CH_2=CHCN$, respectively, at the temperatures studied. In the case of the acetonitrile reaction, no significant variation of the rate of reaction with hydroxyl radicals was observed in the accessible temperature range and the data for all three temperatures studied at 50 torr total pressure are fitted by the single line so labelled in Figure 16.

Table 10 lists the rate constants k obtained by least squares analysis of the data in Figures 14 to 16. In the case of acrylonitrile decay rates were also measured at total pressures of 100 and 500 torr argon at 298 K. As can be seen from Figure 16 and Table 10, the rate constant was ~18% higher at the highest pressure indicating that the reaction proceeds partially or entirely via an addition mechanism and that at room temperature the reaction is in its fall-off region between second order and third order kinetics over the pressure range studied.

The Arrhenius expressions obtained from least squares analyses of the data in Table 10 are given in Table 11 and Figure 17 shows the data for CH_3CN and C_2H_5CN plotted in Arrhenius form. The error bars in Figure 17 represent three times the standard deviation of slopes in Figures 14 and 15, but exclude possible systematic errors contributing to the estimated overall errors listed in Table 10.

Discussion. Variation of the flash energy by a factor of 2 and 4, and hence of the concentration of primary and secondary radicals by this amount, had no observable effect on rates of decay of hydroxyl radicals in

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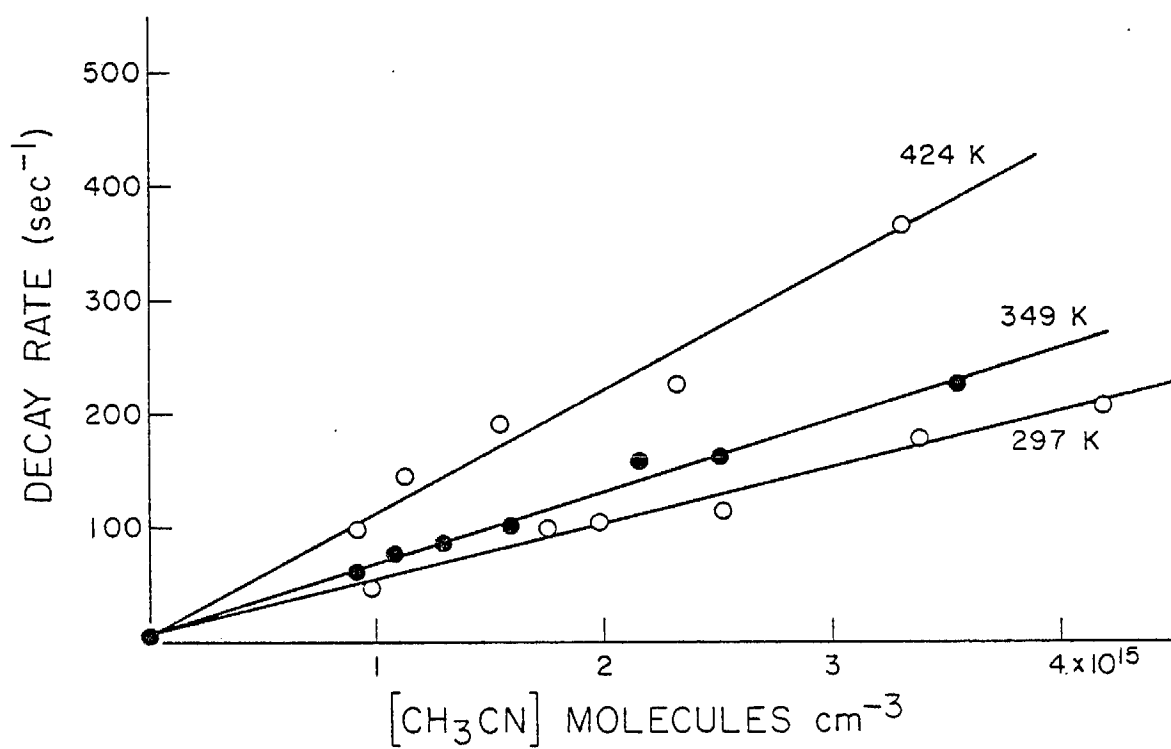
Figure 14. Observed first-order decay rates of OH radicals due to reaction with CH_3CN at three temperatures.
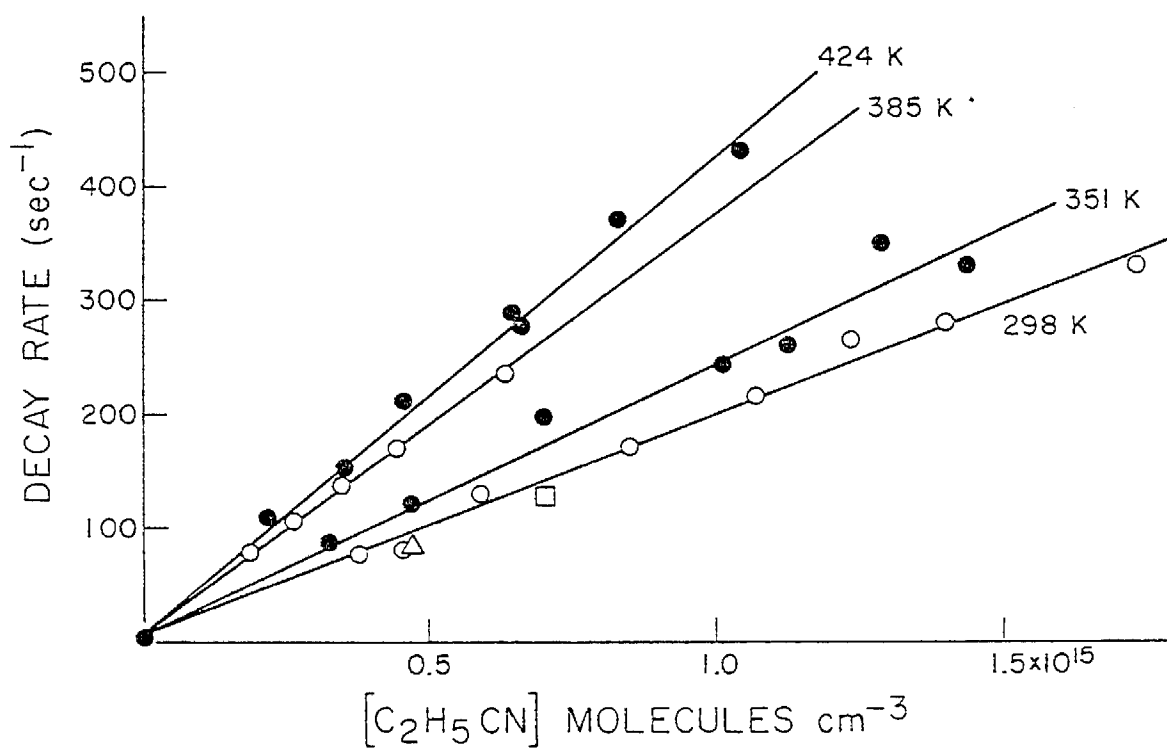
Figure 15. Observed first-order decay rates of OH radicals due to reaction with C_2H_5CN at four temperatures.
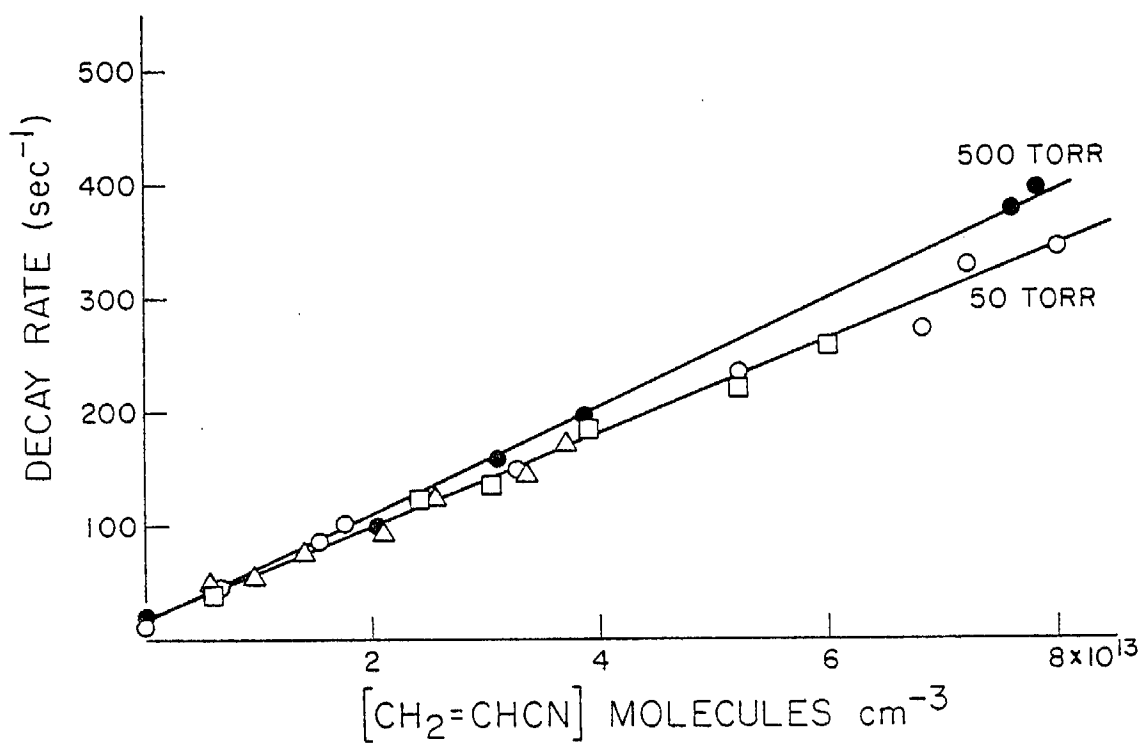
Figure 16. First-order decay rates of OH radicals due to reaction with $CH_2=CHCN$ at 298 K (0), 350 K (Δ), 424 K ($\square$) at 50 torr total pressure and at 298 K ($\bullet$) at 500 torr total pressure of argon.

Table 10. Rate Constants for the Reactions of OH Radicals with Acetonitrile, Propionitrile and Acrylonitrile

Reactant	Temperature K	$10^{13} k$ $cm^3 molecule^{-1} sec^{-1}$ [a]
Acetonitrile	297.2	0.494 ± 0.06
	348.0	0.62 ± 0.07
	423.8	1.05 ± 0.15
Propionitrile	298.2	1.94 ± 0.20
	350.8	2.33 ± 0.25
	384.0	3.62 ± 0.36
	423.0	4.14 ± 0.40
Acrylonitrile	299.0	40.6 ± 4.1
	349.6	40.4 ± 4.1
	422.5	40.2 ± 4.0
	298.7[b]	43.2 ± 4.3
	298.7[c]	48.0 ± 5.0

[a]The indicated error limits are the estimated overall error limits and include the least square standard deviations as well as the estimated accuracy limits of flow meter calibrations, pressure measurements, etc.

[b]Total pressure 100 torr argon.

[c]Total pressure 500 torr argon.

Table 11. Arrhenius Parameters for the Reactions of OH Radicals with Acetonitrile, Propionitrile and Acrylonitrile

Reactant	$10^{13} A$ $cm^3 molecule^{-1} sec^{-1}$	E cal mole^{-1} [a]
Acetonitrile	5.86	1500 ± 250
Propionitrile	26.9	1590 ± 350
Acrylonitrile	40.4 ± 0.45[b]	—

[a]The indicated errors for the Arrhenius activation energies are the estimated overall error limits.

[b]50 torr total pressure argon. No observable temperature dependence.

Figure 17. Arrhenius plot of log k against 1000/T (K) for the
reaction of OH radicals with CH_3CN and C_2H_5CN.

these experiments. This strongly suggests that interference from secondary reactions, or from reactions of OH with products of the photolysis of the reactants, are negligible.

Furthermore, the rates of the reactions of OH with CH_3CN and C_2H_5CN exhibit no dependence upon total pressure and hence the rate constants reported here are applicable to the atmosphere. These may be used to calculate lifetimes due to reaction with OH radicals of ~160 days, ~40 days and ~2 days for CH_3CN, C_2H_5CN and $CH_2=CHCN$, respectively, at 298 K, assuming an atmospheric OH radical concentration of ~1 x 10^6 cm^{-3}. Thus, from these data and the data obtained from the environmental chamber studies, it is obvious that the major atmospheric loss process for these nitriles is reaction with the OH radical, with CH_3CN and C_2H_5CN being less reactive than ethane, but with acrylonitrile reacting at a significant rate under atmospheric conditions.

C. Effect of Added Ammonia on NO_x-Air and NO_x-Air-HNO_3 Irradiations

Since low levels of NH_3 are expected to be emitted in the thermal ammonia injection processes, it is of interest to ascertain the effects of this emitted NH_3 on photochemical air pollution. The simplest and most unambiguously interpreted photochemical system is the irradiated $NO-NO_2$-air system with added propene/propane as a radical trace (see Section IV).

Accordingly, two irradiations were carried out using the SAPRC ~40,000-liter volume outdoor Teflon chamber under dual-mode conditions. These irradiations consisted of (a) an $NO-NO_2$-propene-propane-air irradiation with added NH_3 in one side of the dual-mode chamber, and (b) an $NO-NO_2$-propene-propane-HNO_3-air irradiation with added NH_3 in one side of the dual-mode chamber. The experimental techniques and results are discussed below.

Experimental. The outdoor chamber, constructed from Teflon film, has an initial volume of about 40 m^3 and can be divided into two identical compartments for the purpose of conducting parallel experiments (dual chamber mode) (Figure 18). Teflon was chosen because of its chemical inertness, its low permeability to most chemical species at low concentrations, and its excellent transmission properties. The large volume of the chamber, about 40 m^3 when fully inflated, allows amounts of aerosol to be
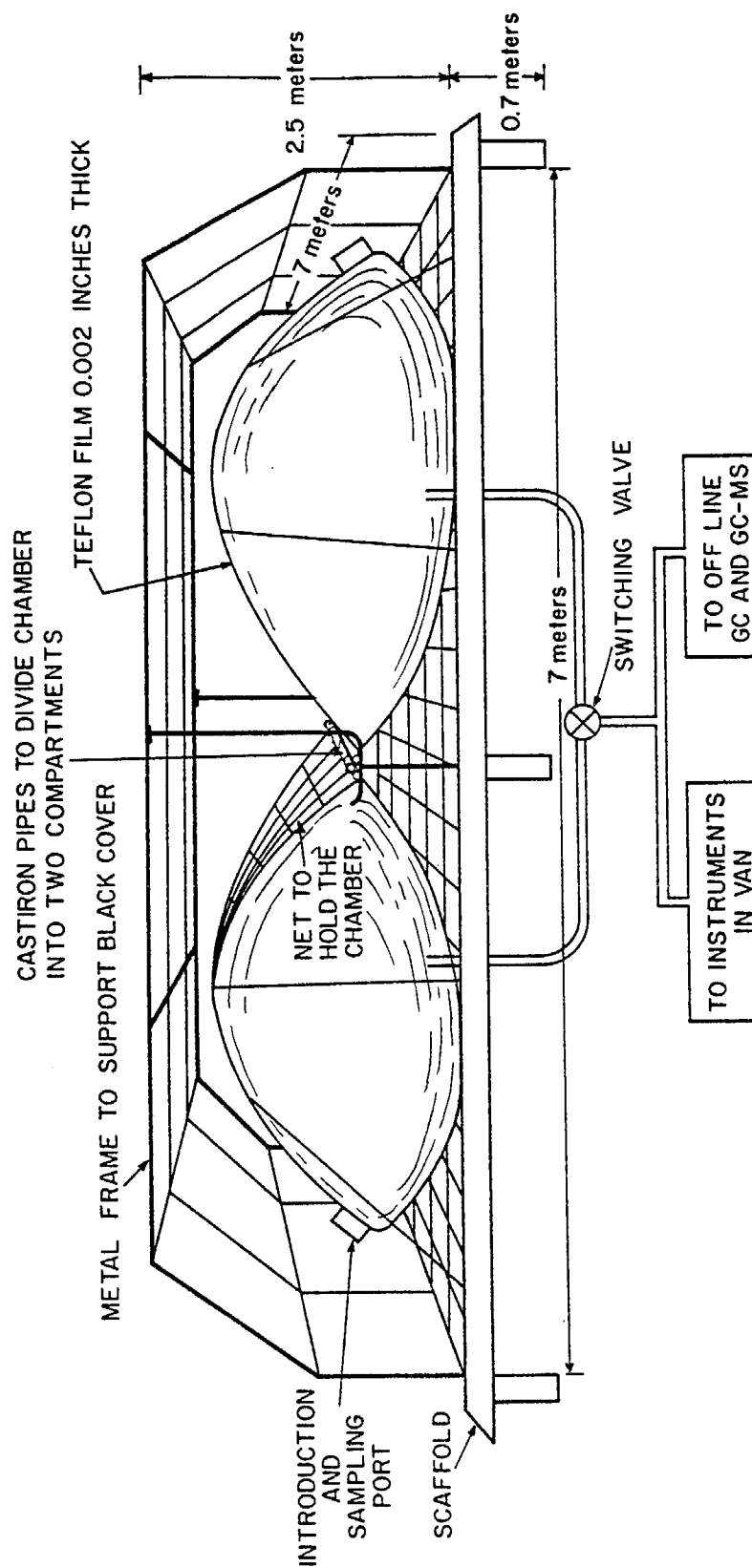
Figure 18. SAPRC 40,000-liter outdoor Teflon chamber.

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generated which are sufficient for complete chemical analysis even for sub-ppm initial concentrations of added pollutants. The large volume also permits gas and aerosol monitoring instruments to be operated continuously throughout the duration of long experiments. Sampling by gas and aerosol monitoring instruments does not affect concentrations because the flexible chamber collapses as air is withdrawn.

The outdoor chamber is constructed of FEP Teflon film sheets (nine panels, each about 30 ft x 60 in x 0.002 in). The panels are heat-sealed together and the seams are externally reinforced with Mylar tape. The chamber is supported by plastic coated wires running across a 25 ft x 20 ft pipe frame held two feet off the ground in order to allow air circulation under the chamber, and is held on the frame by a net connected to the frame by a system of ropes (Figure 18). Wind action on the flexible chamber and the temperature gradient within the chamber are sufficient to ensure adequate mixing during an experiment.

The chamber is immediately adjacent to the ARB Mobile Laboratory, thus allowing continuous monitoring of ambient temperature, relative humidity, and solar radiation intensity during the runs. Each compartment of the chamber has an 8 in x 10 in opening for introduction of ambient or pure air and initial reactants as well as for aerosol sampling during the course and at the end of the experiment.

Monitoring instruments are housed in an air conditioned building and are connected to each chamber compartment through a Pyrex sampling manifold and a 30 ft, 7/16 in i.d. FEP Teflon sampling line equipped with a switching valve. The pollutant transit time from the chamber compartments to the instruments is about 30 seconds.

During a typical run, the following parameters are monitored: NO, NO_2, NO_x (Bendix chemiluminescence instrument), O_3 (Bendix chemiluminescence instrument), CO, hydrocarbon (gas chromatography), peroxacetyl nitrate (electron capture gas chromatography), condensation nuclei (Environmental One counter), light scattering (MRI integrating nephelometer), aerosol size distribution (TSI electrical mobility analyzer and Climet optical particle counter), temperature and dew point.

Changes in solar radiation intensity and spectral distribution are measured using an EG&G integrating spectral radiometer.

Experimental Procedure. The procedure for these runs was as follows. The undivided bag was flushed with pure air for several hours, covered with an opaque cover and then filled with pure air (Doyle et al. 1977) at ~30% RH. NO, NO_2, propene, propane and, for the irradiation involving nitric acid, HNO_3 were injected into the undivided bag. After mixing, the bag was then divided into two compartments (sides A and B) and NH_3 injected into side A sufficient to yield a concentration of ~1 ppm.

The reaction bag was then uncovered and the irradiation carried out for two hours.

Results. For the irradiations carried out, Table 12 gives the initial conditions, Figure 19 and 20 show plots of the log of the propane/propene ratio from which the hydroxyl radical levels are derived (see Section IV), and Table 13 summarizes the hydroxyl radical levels calculated from the slopes of those plots. As seen from Tables 13 and Figure 19 for the irradiated $NO-NO_2$-air mixture with added NH_3 on side A (Run 2), the two sides of the irradiated bag behaved essentially identically, although there was a somewhat higher particulate burden on the added ammonia side, as expected. For the irradiated $NO-NO_2-HNO_3$-air system with and without added NH_3 (Run 3), the data (Table 13 and Figure 20) again show that, within the experimental errors the chemistry occurring is identical, as evident, for example, by the identical hydrocarbon decay rates in sides A and B (Figure 20).

Table 12. Initial Concentrations (ppm) for the Added NH_3 Irradiations

| Reactant | Initial Concentration (ppm) | |
	Run 2	Run 3
NO	0.366	0.399
NO_2	0.150	0.137
Propane	0.0102	0.0107
Propene	0.008	0.009
HNO_3	–	~0.5
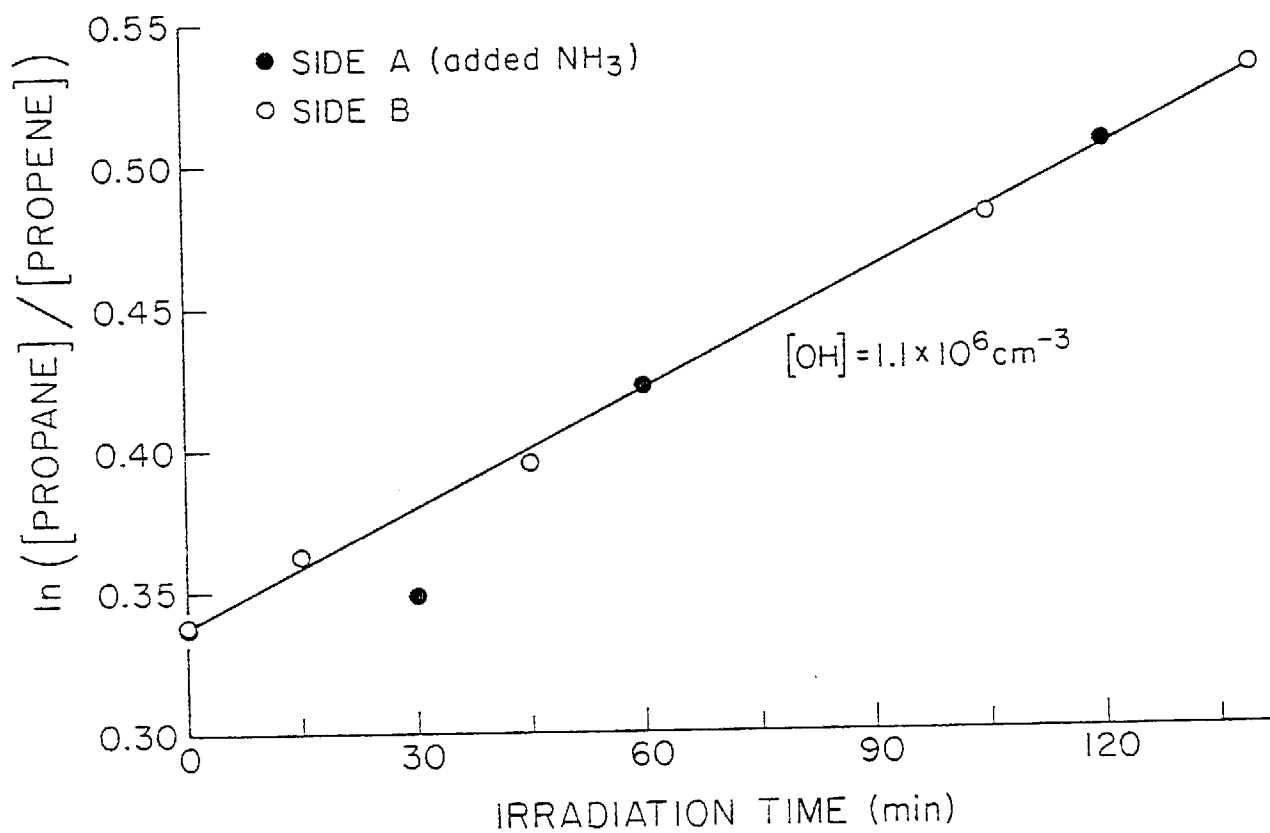
Figure 19. Plots of ln([propane]/[propene]) against irradiation time for NO_x-air (side B) and NO_x-NH_3-air (side A) mixtures with added propane and propene tracers.
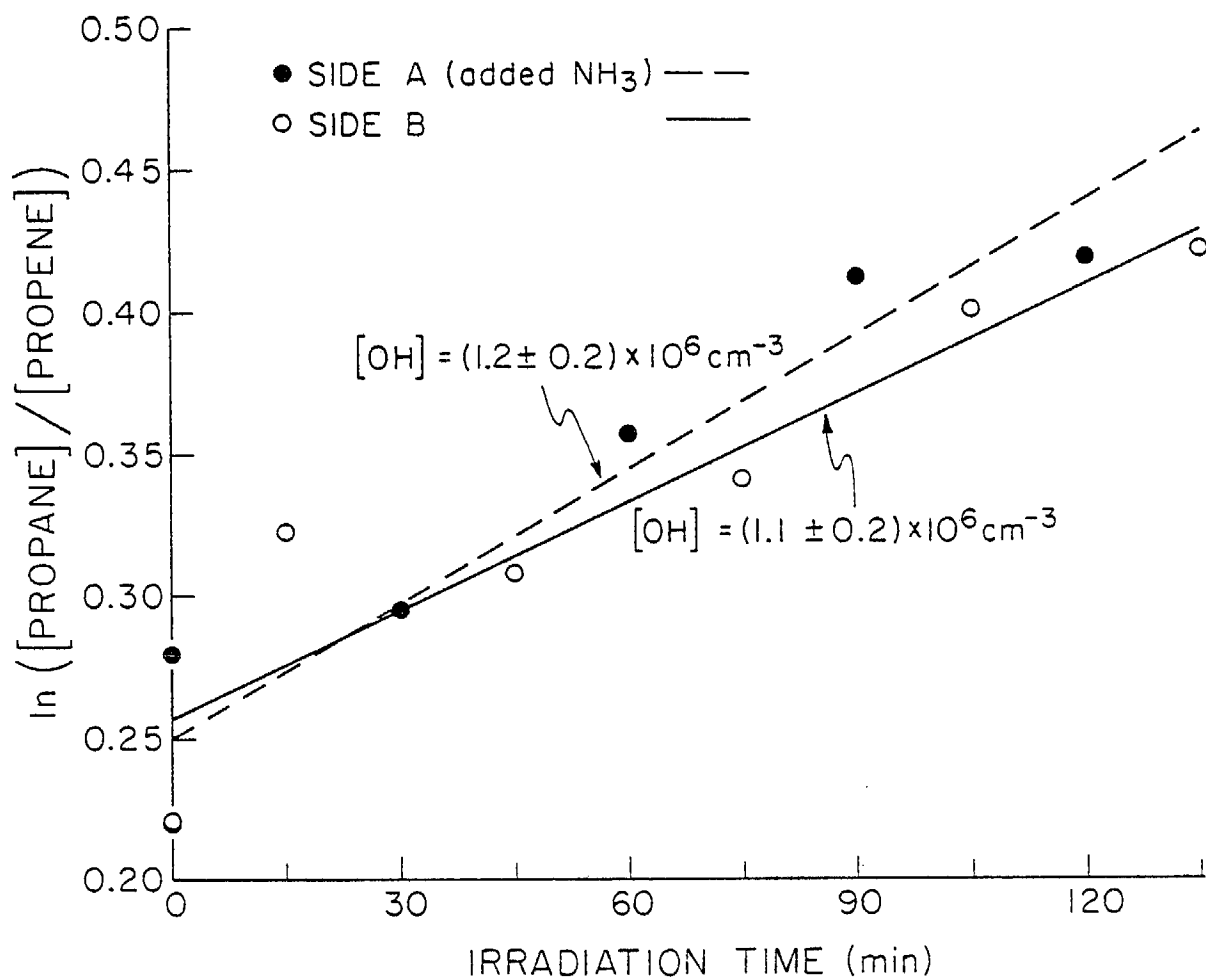
Figure 20. Plots of ln([propane]/[propene]) against irradiation time for
NO-HNO$_3$-air (side B) and NO-NH$_3$-HNO$_3$-air (side A) mixtures
with added propane and propene tracers.

Furthermore, since side A (with added NH_3) had, as expected, substantially higher particulate levels (~50-80 μm^3 cm^{-3} in side A versus 0-2 μm^3 cm^{-3} in side B), it is obvious that the presence of particulates had no effect on the OH radical concentration. As a control experiment, prior to the added NH_3 irradiations, an $NO-NO_2$-air irradiation in the entire (undivided) bag (Run 1) was carried out. As seen from Table 13, the radical levels were, within the analytical accuracy, identical to those obtained in the divided bag with and without added NH_3.

These data imply that: (a) the addition of NH_3 has a negligible effect on radical levels, NO to NO_2 conversion and NO_x loss in irradiated NO_x-hydrocarbon-air systems and (b) the expected increased particulate burden associated with NH_3 emissions (due to $NH_3 + HNO_3 \rightarrow NH_4^+NO_3^-$) also has no observable effect on radical levels, NO to NO_2 conversion or NO_x loss.

Table 13. Hydroxyl Radical Concentrations in Outdoor NO_x-Air Irradiations

Run No.	Conditions	OH Concentration, Radical cm^{-3} [a]	
		Side A	Side B
1	Undivided bag $NO-NO_2$-air	——— 0.93×10^6 ———	
2	Divided bag $NO-NO_2$-air ~1 ppm NH_3 side A	1.1×10^6	1.1×10^6
3	Divided bag $NO-NO_2-HNO_3$-air ~1 ppm NH_3 side A	$(1.2 \pm 0.2) \times 10^6$	$(1.0 \pm 0.2) \times 10^6$

[a]Calculated from the formula

$[OH] = (k_2-k_1)^{-1}d\ln([\text{propane}]/[\text{propene}])/dt,$

where k_1 and k_2 are rate constants for the reaction of OH with propane and propene, respectively (Atkinson et al., 1979).

III. AN EXPERIMENTAL INVESTIGATION OF OFFGASSING OF NITROGENOUS
COMPOUNDS IN THE SAPRC 5800-LITER CHAMBER

For the past several years, under funding from the California Air Resources Board and other agencies, we have been studying the effects of a variety of physical parameters on the formation of simulated photochemical smog. In a previous SAPRC-ARB chamber program (Contract No. A7-175-30), a series of experiments were carried out in the 5800-liter evacuable chamber to determine the effects of temperature on smog formation. These experiments involved irradiations of surrogate hydrocarbon-NO_x-air mixtures and (for control purposes) alkane-NO_x-air mixtures in the 5800-liter evacuable chamber at 282, 303 and 323 K under controlled conditions, including a constant water concentration of 5×10^3 ppm. The results of those experiments indicated that radical levels and ozone yields increase significantly as the temperature increased. Furthermore, for most of the runs carried out at 323 K, the total NO_x consumption rates were considerably less than expected based on the known NO_x removal reactions, and in one experiment the total monitored NO_x levels actually increased. It is not clear how such observations can be accounted for by homogeneous gas phase chemical processes, and the possibility of their being due entirely to heterogeneous or chamber effects cannot be eliminated.

Clearly, before these and other evacuable chamber irradiations can be reliably used for model validation or for assessing the effects of various parameters on smog formation, the role of chamber effects in influencing such data must be elucidated. In Section IV of this report, results of an extensive series of experiments aimed at studying chamber effects related to radical initiation are described. In this section, results of preliminary and exploratory experiments aimed at studying NO_x offgassing in the SAPRC 5800-liter evacuable chamber are described.

Development of Improved NO-NO_x-HNO_3 Continuous Analysis Techniques. It is now recognized that HNO_3 can be converted to NO by the molybdenum converters employed in commercial NO-NO_x analyzers (Winer et al. 1974, Spicer and Miller 1974, Joseph and Spicer 1978). Thus, providing that HNO_3 is not removed by the sample lines, the instrumental NO_x-NO readings will include HNO_3, as well as peroxyacetyl nitrate (PAN), organic nitrates

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etc., along with NO_2 levels. In order that the NO_x data in this study be better characterized, an investigation was first carried out to determine the extent of HNO_3 interference, and whether this inference could be used as a basis for a reliable HNO_3 monitoring technique.

Several experiments were performed which confirmed the results of Joseph and Spicer (1978) that cartridges packed with nylon wool can efficiently remove HNO_3 from the gas sample stream without affecting NO, NO_2, or PAN levels. These nylon filters were then used to show that although the Teflon sample lines employed in our past $NO-NO_x$ analyses effectively removed HNO_3 under conditions of relatively low levels of NO_x (< 1 ppm), HNO_3 interference became significant under conditions where with higher NO_x concentrations were employed. It is also possible that the sample lines become less efficient in removing HNO_3 at higher temperatures, but this aspect was not tested. Therefore, in order to remove any ambiguities in our NO_x data due to the variable efficiencies of the sample lines in removing HNO_3 prior to its entering the molybdenum converter, our $NO-NO_x$-analysis procedures were modified by the routine incorporation of nylon filters in the $NO-NO_x$ sample line, with these filters being replaced at periodic intervals.

A considerable amount of effort was expended in an attempt to develop a reliable continuous HNO_3 analyzer based on modified chemiluminescence $NO-NO_x$ analyzers such as those described by Kelly et al. (1979) and by Joseph and Spicer (1978). Several modifications of a commercial TECO 14B/E instrument were carried out. In all cases, the molybdenum converter was removed from the instrument housing and placed as close to the chamber as possible in order to minimize HNO_3 losses on sample lines.

In the first configuration tried, shown in Figure 21a, the solenoid selected whether the flow went through the nylon filter ("NO" mode) or bypassed the filter ("NO_x" mode), prior to entering the converter, allowing (in principle) HNO_3 to be read as "NO_2", i.e. the difference between the "NO_x" and the "NO" channel. However, this configuration was not successful; when HNO_3 was in the chamber, both "NO_x" and "NO" readings were identical in the automatic (alternating) mode, despite the fact that the readings for a continuous flow through the filter ("NO" manual mode) were considerably less than when the flow continuously bypassed the filter

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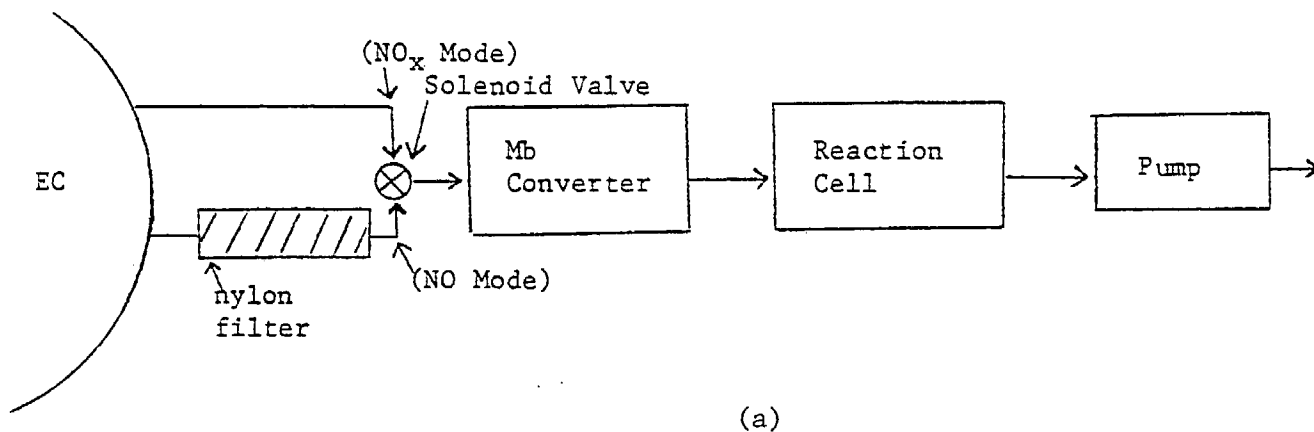
(a)
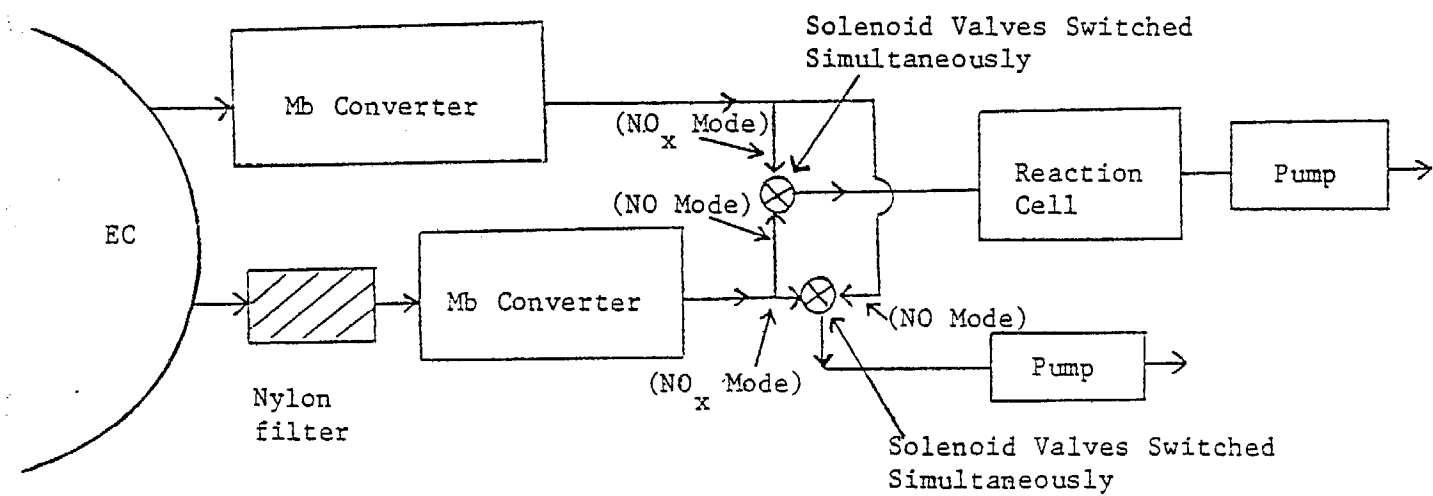
(b)

Figure 21. Schematic of configurations used to monitor nitric acid.

("NO$_x$" manual mode). It was also observed that it required more than five to 10 minutes for HNO$_3$ to attain equilibrium with respect to absorption and desorption on the sample line, which is far longer than the 30-second alternating modes of the NO-NO$_x$ analyses.

Attempts were made to avoid this HNO$_3$ absorption/desorption problem by converting the HNO$_3$ to NO$_2$ using heated glass beads prior to its entering the common sample line leading to the molybdenum converter. However, despite the fact that Kelly et al. (1979) apparently were successful in using heated glass beads as an HNO$_3$ to NO$_2$ converter, we found that the glass beads irreproducibly adsorbed and/or destroyed NO$_x$ and HNO$_3$, and after several attempts to correct this by cleaning or conditioning them, their use was abandoned.

The most successful configuration tried is shown in Figure 21b. In this case the common sample line was eliminated by employing a second molybdenum converter (taken from another TECO NO-NO$_x$ instrument in our laboratory) to convert the HNO$_3$ to NO, with a continuous gas flow through both the unfiltered and filtered converter being achieved by using two solenoids simultaneously switched to select which gas flow goes to the detector and which is discarded. This configuration eliminated the problem caused by HNO$_3$ absorption and desorption, and the readings obtained on the automatic (alternating) mode were found to be consistent with those in the manual modes, with the unfiltered channel giving appropriately higher readings than the filtered channel when HNO$_3$ was present in the gas being sampled. However, it was found that the output of the two converters gave different readings when the gas being sampled contained no HNO$_3$ or when no nylon filters were employed; and when the nylon filter was switched from one converter to the other, different results were obtained. These discrepancies generally amounted to 10 to 20% of the total NO$_x$ and appeared to be worse when the gas being sampled was humidified. This problem is probably inherent in the use of molybdenum converters for NO$_x$ monitoring, and all NO$_x$ data obtained using this technique must be considered to be uncertain by at least 10 to 20%.

Chamber Offgassing Experiments. Two sets of offgassing experiments were conducted. One set was carried out with the chamber in a relatively contaminated condition following a series of dark experiments which involved

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injecting O_3 (0.1-1 ppm), NO_2 (5-10 ppm), phenols and other aromatics (~0.1 ppm) and alkenes (~0.1 ppm) in 1 atm air in the chamber (Carter et al. 1981). The other set followed an overnight evacuated bakeout ($\leq 10^4$ torr at 366 K) of the chamber. In both sets of experiments, the chamber was filled with pure air at ~5% RH and oxides of nitrogen were monitored using both the modified (see Figure 21b) and an unmodified TECO $NO-NO_x$ analyzer. The chamber temperature was held first at ~303 K, then at ~328 K, and finally at ~363 K. At the highest temperature, gas samples were taken for gas chromatographic analysis of organics.

Additional experiments were carried out utilizing the capability of our differential UV-visible spectrometer (DUVVS) interfaced to the chamber (see Figure 22) to monitor the possible formation of nitrous acid (HONO). This system has been used previously in our long path studies of trace species in the ambient air, and is described in detail elsewhere (Platt et al. 1980a,b). For this study, a 75 watt xenon high pressure point source arc was mounted at the solar simulator end of the chamber, with the spectrometer at the opposite end. Two flat mirrors were mounted on each end of the chamber to achieve a five-pass, 20-meter pathlength. HONO was monitored using its absorption bands at 365 and 348 nm, after subtraction of the NO_2 absorptions at those wavelengths using a standard NO_2 spectrum. The detection limit of HONO with this configuration was ~20 ppb.

The offgassing rates obtained using the modified and unmodified $NO-NO_x$ instruments are summarized in Table 14 for experiments carried out both before and after the evacuated bakeout. It can be seen that before the evacuated bakeout, NO_x offgassing occurred at 303 K and increased dramatically as the temperature was increased. After the evacuated bakeout, offgassing was still significant at the higher temperatures, but was a factor of ~3 lower than before. At 303 K the NO_x levels actually decreased from the background present in the pure air fill, indicating that NO_x absorption onto the walls was probably occurring.

Contrary to our initial expectations, offgassing of NO_2 was insignificant even in the contaminated chamber, since the offgassed material consisted primarily of NO and some nitrogenous material which was converted to NO by the molybdenum converter, and which was trapped by nylon. This material is probably primarily HNO_3; if HONO was formed, it was at levels less than

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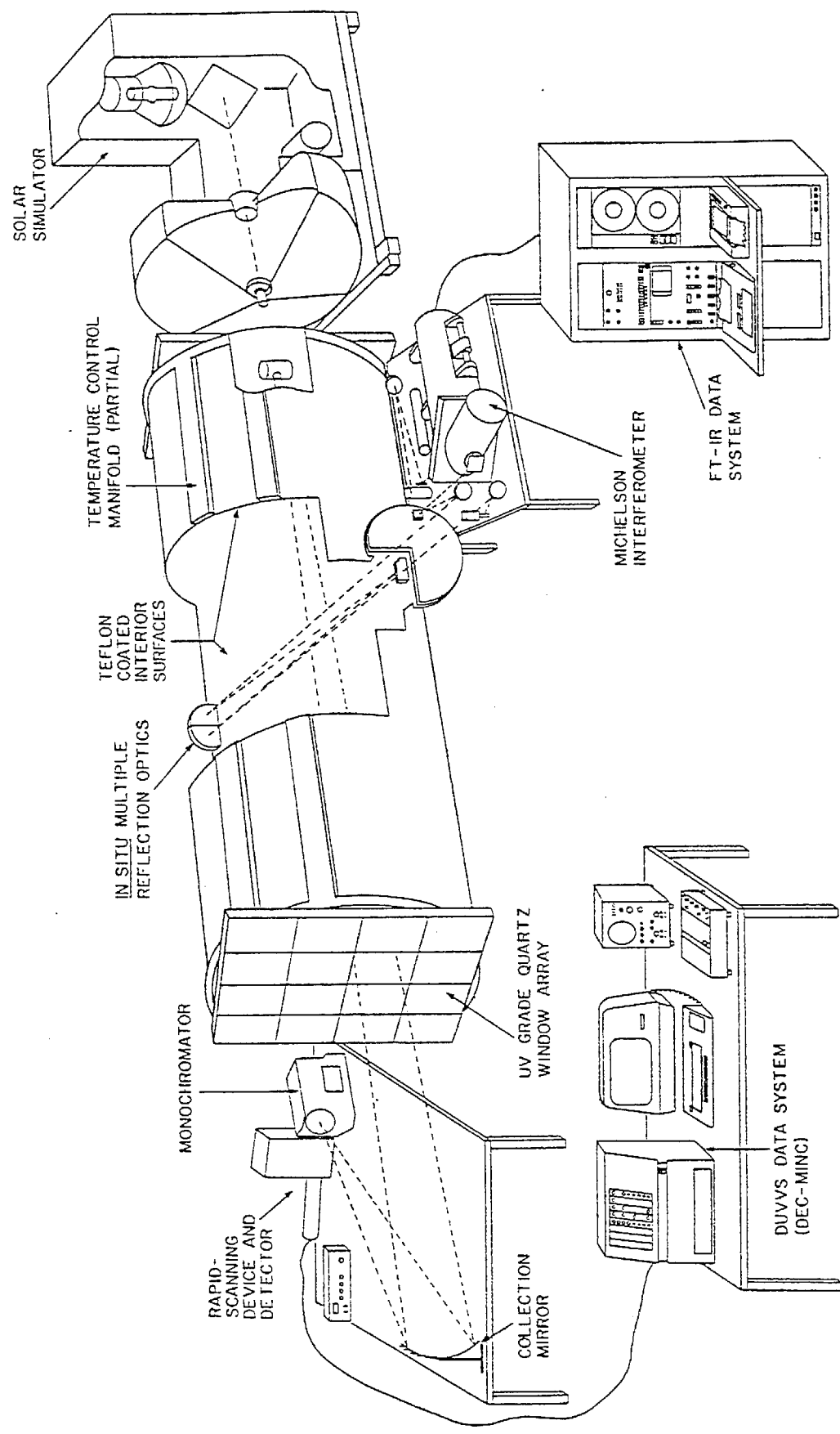
Figure 22. SAPRC 5800-liter evacuable chamber with interfaced long path FT-IR and DUVVS system.

SOLAR SIMULATOR

TEMPERATURE CONTROL MANIFOLD (PARTIAL)

TEFLON COATED INTERIOR SURFACES

IN SITU MULTIPLE REFLECTION OPTICS

MONOCHROMATOR

RAPID-SCANNING DEVICE AND DETECTOR

COLLECTION MIRROR

UV GRADE QUARTZ WINDOW ARRAY

MICHELSON INTERFEROMETER

FT-IR DATA SYSTEM

DUVVS DATA SYSTEM (DEC-MINC)

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Table 14. Offgassing Rates (ppb hr^{-1}) of Nitrogenous Compounds in the SAPRC Evacuable Chamber

Conditions	Unmodified TECO[a]			Modified TECO	
	NO	NO$_2$	NO$_x$	NO$_x$[a]	NO$_x$ + Nitrate[b]
Before Evacuated Bakeout					
303 K	0.3	0	0.3	0.3	0.8
328 K	2.4	0	2.4	2.4	~10
363 K initial	78	0	78	70	140
final[c]	69	0	69	62	84
After Evacuated Bakeout					
303 K	−0.2	—	—	−0.02	−0.6
328 K	0.7	—	—	—	—
363 K	27	4	31	18	34

[a]Nylon filter in line.
[b]No nylon filter; "nitrate" is presumed to be HNO$_3$.
[c]Approximately four hours after 363 K temperature attained.

the ~20 ppb sensitivity of the DUVVS system for most of these experiments. HONO was only detected in one experiment in which the chamber was held at ~363 K overnight. In that run, a trace (~20 ppb) of HONO was detected using the DUVVS system.

In order to determine the extent of offgassing of organic materials at high temperatures, samples were taken for gas chromatographic analyses during both of the 363 K temperature offgassing runs. A variety of chromatographic columns, employing both flame ionization and electron capture detection were used. In both experiments, no significant increase in organic material over the background levels characteristic of our pure air were observed, even when a total carbon analyzer was employed.

Following the offgassing determinations at ~363 K, the chamber contained ~0.4 ppm of NO and ~0.2 ppm of material (presumed to be HNO_3) in the first set of experiments, and ~0.1 ppm each of NO and "HNO_3" after the evacuated bakeout. In both cases, the mixtures were left in the chamber overnight as it cooled to ambient temperature. In both sets of experiments, the NO and HNO_3 levels declined during these periods, with the NO decreasing after the first run by ~15% and the HNO_3 decreasing by ~65% as a result of cooling the chamber from ~363 K to ~303 K (data at 303 K was not available for the second run since the mixture was immediately reheated to 363 K the following day, but the initial HNO_3 levels in the reheated mixture was at least ~50% lower than the final levels on the previous day). It is thus apparent that the material assumed to be HNO_3 has a tendency to be reabsorbed on the walls at lower temperatures.

As has been shown in other chambers (Jeffries 1977), these experiments demonstrate that offgassing of nitrogenous species can be significant in the SAPRC evacuable chamber especially at elevated temperatures, and that this offgassing is reduced, but not eliminated, by an evacuated bakeout of the chamber. The major species offgassed appear to be NO and HNO_3, with lesser amounts of NO_2 being observed. The nature and chemical or physical mechanism of this effect is presently unknown, but clearly it must be taken into account in the analysis of data from runs carried out at elevated temperatures in chambers with Teflon coated interiors.

IV. AN EXPERIMENTAL INVESTIGATION OF CHAMBER DEPENDENT RADICAL SOURCES

An important aspect of the development of reliable computer models for the formation of photochemical smog is their validation against smog chamber data. This requires not only a complete understanding of the kinetics and mechanisms of the chemical reactions which occur during the photooxidations of part-per-million (ppm) concentrations of NO_x and organics in air, but also an adequate and quantitative understanding of major chamber effects.

At the present time, although detailed mechanisms of the NO_x photo-oxidations of certain alkanes, alkenes and aromatics are qualitatively or semi-quantitatively accurate, all such recent computer models have invoked the presence of an as yet unknown source of radicals in order to match computer-predicted time-concentration profiles with the results of smog chamber experiments (Hendry et al. 1978, Falls and Seinfeld 1978, Carter et al. 1979a, Whitten et al. 1979, 1980; Atkinson et al. 1980).

To date, modelers have differed on how best to represent this radical source in their mechanisms, although it is generally assumed to be chamber dependent. In recent studies, Falls and Seinfeld (1978) and Whitten et al. (1979, 1980) have used only initial nitrous acid (HONO) (presumed to be formed heterogeneously during the injection of NO_x), while Carter et al. (1979a) and Atkinson et al. (1980) have used a constant radical flux, and Hendry et al. (1978) have used a combination of the two. These approaches are significantly different, since the use of initial HONO leads to a rapidly decreasing radical flux, while a constant radical source results in a considerably greater total radical input during a typical environmental chamber irradiation.

Clearly, aspects of the photochemical mechanisms relating to radical initiation and termination processes cannot be unambiguously validated using smog chamber data until this presently poorly characterized radical source is elucidated. Despite previous studies of "dirty chamber effects" (Wu et al. 1976; Bufalini et al. 1972, 1977), no systematic investigation of chamber-dependent radical sources has been reported to date. In the present study, a series of NO_x-air irradiations have been carried out under a variety of conditions and in four environmental chambers in order

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to investigate more directly the characteristics and magnitude of this excess radical initiation effect.

Experimental. The experiments consisted of NO_x-air irradiations carried out in four different environmental chambers employing different light sources. Initial NO concentrations ranged from ~0.1 to 1.8 ppm and initial NO_2 from ~0.05 to 0.5 ppm, and in order to monitor hydroxyl radical levels, ~10 ppb each of propene and propane were included in the reaction mixture. Hydroxyl radical levels were determined from the rate of decrease of the propene/propane ratio, based on the assumption that reaction with OH is the only significant loss process for these species (see discussion). Thus,

$$[OH] = (k_{21}-k_{22})^{-1} \, d\ln([propane]/[propene])/dt$$

where k_{21} and k_{22} are the rate constants for the reaction of OH radicals with propene and propane, respectively (see later). The use of this ratio technique eliminates the necessity to correct for dilution due to sample withdrawal from the chamber and avoids errors due to differences in sample sizes since both species are analyzed on the same gas chromatographic column, as has been discussed previously (Atkinson et al. 1978).

The chambers and experimental techniques employed in this study were as described below:

(1) The majority of irradiations were carried out in the SAPRC 5800-liter evacuable, thermostatted, Teflon-coated environmental chamber equipped with a 25 KW solar simulator (Figure 23). The characteristics and operating procedures of this environmental chamber-solar simulator facility have been described in detail previously (Winer et al. 1980), and only the pertinent details will be briefly discussed here.

The solar simulator, employing a 25 KW point source xenon arc, provides a well-collimated light beam which, to a large extent, does not illuminate the chamber walls, thus minimizing wall photochemistry. In all experiments reported here, a 1/4 inch Pyrex pane was used to obtain a spectral distribution applicable to that in the lower troposphere. The light intensity within the chamber was routinely monitored by measuring the rate of photolysis of NO_2 in N_2 (k_1) by the method described by Holmes et al. (1973) with updated rate constants (Hampson and Garvin 1978).
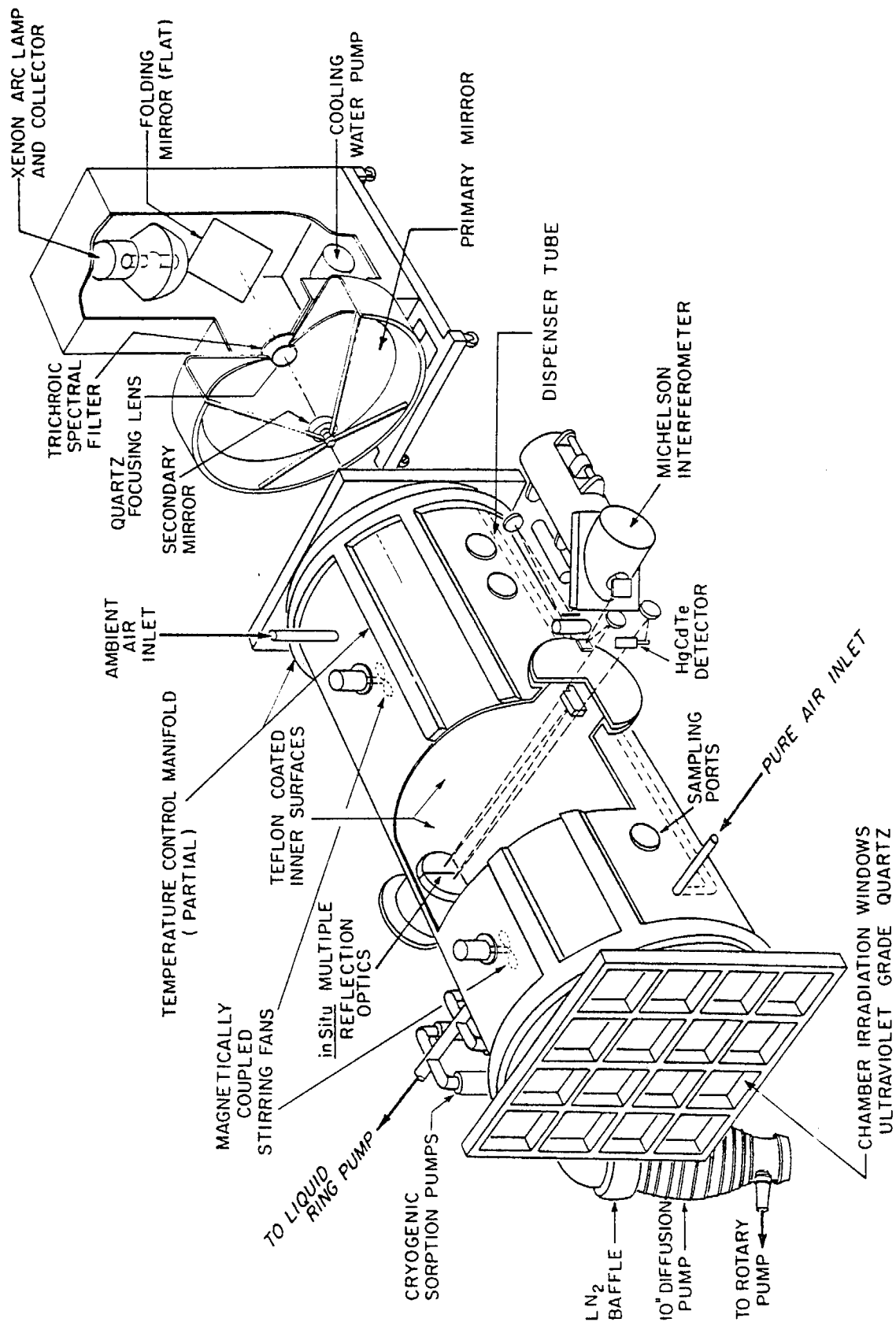
Figure 23. SAPRC 5800-liter evacuable chamber-solar simulator facility.

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Between irradiations the chamber was evacuated overnight to $\leq 10^{-5}$ torr (Winer et al. 1980). For the majority of experiments, the chamber was initially filled to ~10 torr with dry N_2, and then NO and NO_2 were flushed into the chamber from an ~5-liter Pyrex bulb attached to a vacuum line by a stream of ultra-high purity nitrogen. The NO was purified by passage through a trap containing activated Linde Molecular Sieve 13X, while NO_2 was prepared by reaction of this purified NO with O_2 which had also been passed through activated Molecular Sieve 13X. After the NO_x injection, the chamber was filled to ~740 torr with purified matrix air (Doyle et al. 1977, Winer et al. 1980), and the propene and propane tracers were injected using gas-tight all-glass syringes and were flushed into the chamber with N_2.

For the 0% relative humidity (RH) runs and certain 100% RH runs, special procedures were used during the air fill. In the dry runs, the chamber was filled to ~150 torr with the evaporate from liquid O_2, and then filled up to atmospheric pressure with the evaporate from liquid N_2. In order to obtain water saturation in the 100% RH, high temperature run, the requisite quantity of liquid water was injected into the heated, evacuated chamber prior to the pure air fill. For the 100% RH runs at lower temperatures, the purified matrix air was humidified at a temperature higher than that of the chamber.

NO and NO_2 were monitored using continuous commercial NO-NO_x analyzers fitted with a nylon filter in the sample line to remove possible HNO_3 interferences in the NO_2 analysis (see Section III). Although O_3 was not expected to be formed to any measurable extent in these runs, this was verified for most runs using a commercial UV absorption O_3 monitor. Propene, propane and background levels of other organics and CO were monitored by gas chromatography (Pitts et al. 1979a), and formaldehyde was monitored by an improved chromatropic acid method (Pitts et al. 1979a).

(2) A more limited set of irradiations was carried out in the SAPRC ~6000-liter all-Teflon (FEP, 2 mil thickness) chamber (Figure 24). Irradiation was provided by two diametrically opposed banks of 40 Sylvania 40-W BL lamps, backed by arrays of Alzak-coated reflectors. The light intensity in the chamber was controlled by switching off sets of lights as previously described (Darnall et al. 1981), and the light intensities for
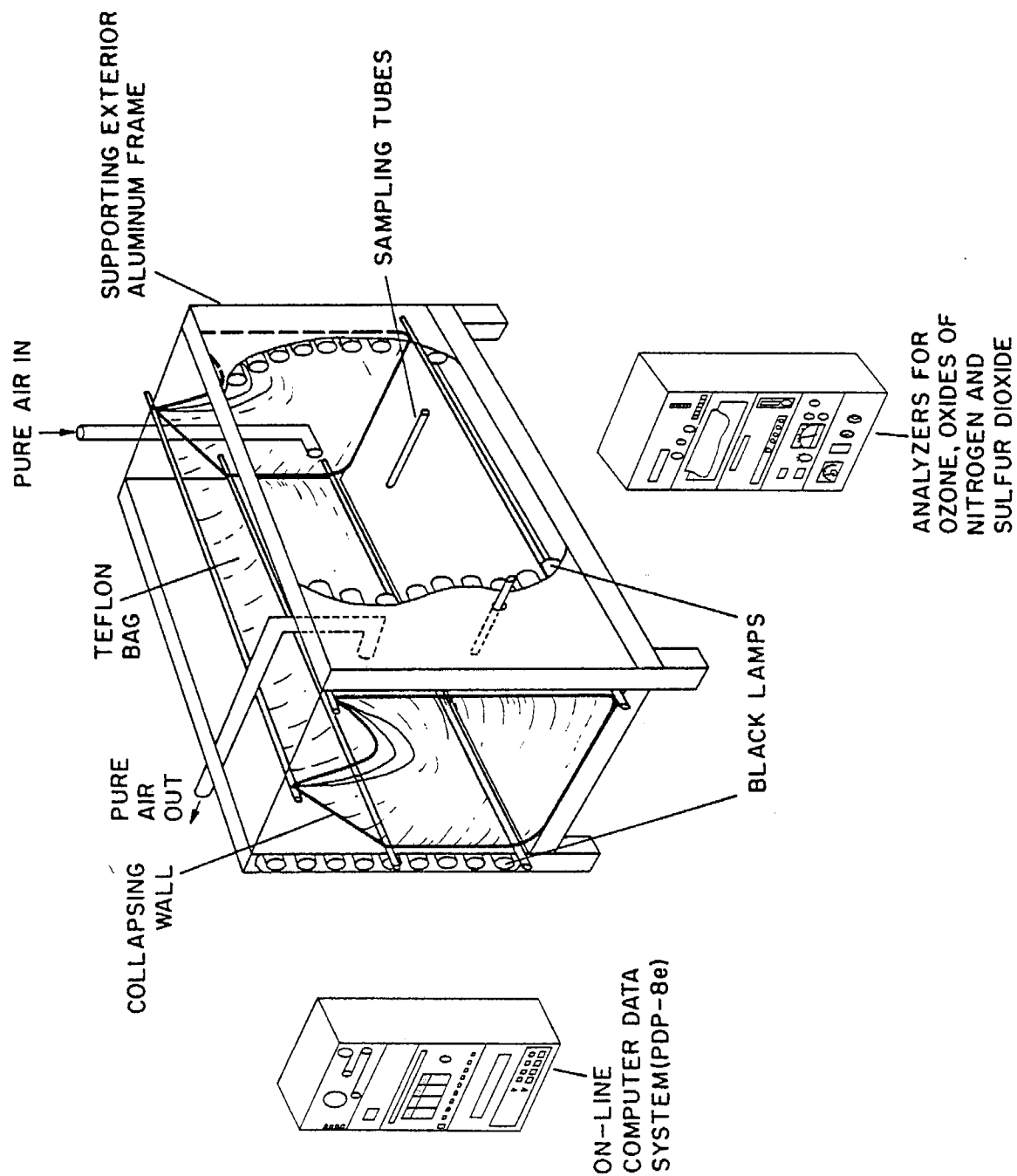
Figure 24. SAPRC 6000-liter indoor all-Teflon environmental chamber.

the various levels of illumination were monitored (Pitts et al. 1979b) by measuring the rate of photolysis of NO_2 in N_2 using the quartz-tube, continuous flow technique of Zafonte et al. (1977).

Before each experiment, the chamber was flushed with dry purified air (Doyle et al. 1977) for ~2 hours at a flow rate of ~12 cfm, and then with air at the desired relative humidity for ~1 hour. All starting materials were injected using gas-tight all-glass gas syringes and were flushed into the chamber using dry ultra-high purity N_2. Commercially available tank NO (Matheson, CP grade, 99.0%) was used without further purification, and NO_2 was prepared by diluting this NO with dry, pure O_2 in a syringe. The analytical procedures employed were the same as used for the 5800-liter evacuable chamber runs (see above).

(3) Several irradiations were carried out in ~40,000-liter outdoor Teflon (FEP, 2 mil thickness) chambers with natural sunlight irradiation. The techniques used (Section II) were generally similar to those used for the indoor all-Teflon chamber described above, except that prior to irradiation the chamber was covered with an opaque cover. The light intensity was monitored using a UV radiometer.

(4) A few irradiations were also carried out using a 100-liter Teflon (FEP, 2 mil thickness) bag, irradiated with an array of fluorescent lamps yielding an NO_2 photolysis rate k_1 of 0.27 min^{-1}. In this system NO and NO_2 and the propane and propene were injected into the bag by gas-tight, all-glass gas syringes, and the bag was then filled with ultra-high purity dry air. The light intensity was monitored by measuring the photolysis rate of NO_2 in N_2 as described above for the indoor Teflon chamber.

The physical characteristics of the four chambers employed in this study are summarized in Table 15.

Results and Discussion. Tables 16 through 19 give the experimental conditions and observed NO conversion rates and initial and final OH radical levels for all of the experiments carried out in this study. Plots of ln([propane]/[propene]) vs. time, from whose slopes the hydroxyl radical concentrations are derived, are shown in Figures 25 and 26 for several representative runs. In general, as seen from Figures 25 and 26, for runs at T ≤ 303 K, RH ≤ 50% and [NO]/[NO_2] > 1, the OH radical levels remained

Table 15. Physical Characteristics of the Four Chambers Used

	Evacuable Chamber	Indoor Teflon Chamber	Outdoor Teflon Chamber	Teflon Bag
Location	Indoors	Indoors	Outdoors	Indoors
Volume (liters)	5800	~6000	~40,000	~100
Surface Material	Teflon (TFE)-coated aluminum	FEP Teflon	FEP Teflon	FEP Teflon
Irradiation Source	Xenon arc	Fluorescent blacklights	Sunlight	Fluorescent blacklights
NO_2 Photolysis Rate (k_1)	0.49 min^{-1}	~0.45 min^{-1}	~0.3 min^{-1}	~0.27 min^{-1}
Intensity Profile	Constant	Constant	Diurnal	Constant
NO_x Injection Technique	Vacuum	Syringe	Syringe	Syringe

Table 16. Conditions and Selected Results for Evacuable Chamber NO$_x$-Air Irradiations

EC Run No.	Run Cond-tions[a]	T (K)	RH (%)	Initial NO (ppm)	Initial NO$_2$ (ppm)	Average [OH] (10^6 Radicals cm^{-3}) 0-60 min	Average [OH] 60-120 min	Radical Flux (ppb-min^{-1})	-d[NO]/dt[b] (ppb min^{-1}) Obs.	Calc.	Obs-Calc	Est.[c] Init. HONO (ppb)
453		284.5	~0	0.403	0.109	1.5	1.7	0.09	0.16	0.17	-0.01	3
452		284.7	~50	0.375	0.091	2.0	2.2	0.10	0.18	0.19	-0.01	4
454		284.0	~100	0.373	0.081	4.4	5.0	0.21	0.24	0.52	-0.28	8
455	A	283.4	21	0.120	0.360	3.0	2.0	0.28	0.16	0.29	0.13	16
443		303.0	~0	0.411	0.099	2.5	2.7	0.17	0.15	0.24	-0.09	4
444		303.6	~0	0.413	0.114	2.4	2.3	0.16	0.49	0.22	0.27	
434		302.6	40	0.398	0.075	4.2	4.3	0.31	0.59	0.47	0.12	
435		303.9	40	0.382	0.087	4.3	4.6	0.31	0.35	0.36	-0.01	
441	(Std)	303.4	45	0.431	0.104	5.3	3.9	0.30	0.67	0.53	0.14	7
457		303.4	~45	0.403	0.093	3.9	4.3	0.27	0.45	-	-	10
462		303.4	~45	0.409	0.096	3.9	3.6	0.26	0.36	0.50	-0.14	
446		303.1	~80	0.387	0.059	12.2	10.6	0.71	0.62	0.89	-0.27	
445		304.2	100	0.411	0.049	16.8	12.1	1.20	0.67	1.54	-0.87	15
437	A	304.1	42	0.160	0.040	4.2	5.2	0.20	0.35	-	-	1.5
464	A	~303.0	~45	0.100	0.093	5.3	4.3	0.25	0.23	-	-	7
440	A	303.0	45	0.674	0.084	3.2	4.2	0.28	0.67	0.48	0.19	3
438	A	302.3	43	0.131	0.469	4.2	3.3	0.57	0.47	-	-	
442	A	302.9	52	0.117	0.369	7.3	3.7	0.56	-0.01	-	-	50
465	A	302.7	~45	0.399	0.371	3.1	2.4	0.44	-0.21	0.18	-0.39	

(continued)

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Table 16 (continued) – 2

EC Run No.	Run Conditions[a]	T (K)	RH (%)	Initial NO (ppm)	Initial NO2 (ppm)	Average [OH] (10^6 Radicals cm^{-3}) 0-60 min	60-120 min	Radical Flux (ppb min^{-1})	-d[NO]/dt[b] (ppb min^{-1}) Obs.	Calc.	Obs-Calc	Est.[c] Init. HONO (ppb)
436	A	302.7	45	1.426	0.364	2.6	2.5	0.51	0.39	–	–	15
458	B	302.7	~45	0.379	0.081	4.6	4.9	0.28	0.39	–	–	
459	C	303.0	~45	0.354	0.100	4.7	4.8	0.28	0.27	0.24	0.03	
463	D	302.1	~45	0.326	0.172	2.7	2.9	0.29	0.23	–	–	
460	E	302.2	~45	0.409	0.063	8.5	5.4	0.35	0.55	0.27	0.28	
462	A,B,F	305.6	~45	0.356	0.117	3.7	3.0	0.49	0.01	–	–	
463	A,B,G	302.0	~45	0.310	0.146	2.7	2.3	0.38	0.08	0.20	-0.12	
439	H	303.1	~0	0.387	0.081	7.6	5.2	0.23	0.20	0.59	-0.39	
469	B,I	302.8	~30	0.368	0.104	3.9	3.6	0.27	0.50	0.18	0.32	
458	J	302.4	~45	0.405	0.083	2.1	2.6	0.14	0.19	–	–	
457	B,J	302.9	~45	0.371	0.095	2.5	2.6	0.18	0.24	–	–	
469	I,J	302.8	~30	0.399	0.104	2.3	2.2	0.15	0.23	0.16	0.07	
449		~323.0	~0	0.45	0.110	5.7	5.7	0.44	0.28	0.37	-0.09	8
448		323.4	~50	0.427	0.055	16.5	11.7	1.32	1.18	0.50	0.68	25
447		323.0	~50	0.442	0.071	13.6	12.6	1.50	1.17	0.54	0.63	>100
450		324.5	100	0.597	0.140	29.5	9.6	1.78	0.96	0.39	0.57	
451	A	325.3	~50	0.148	0.241	15.1	7.8	1.18	0.37	0.23	0.14	

aCodes for special run conditions are as follows:

A – Nonstandard NO or NO2 levels.

B – Second two hours of a two-part run. (If not specified for a two-part run, data given is for first two hours.)

C – Syringe injected NOx.

D – NO2 prepared by reacting O3 with NO in the chamber.

(continued)

Table 16 (continued) - 3

E - NO injected into EC 27 hours prior to run. NO_2 not injected.
F - O_3 added to reaction mixture to convert NO to NO_2 at the beginning of the second part of this run.
G - NO_2 added to the reaction mixture at the beginning of the second part of this run.
H - Immediately follows evacuated bakeout of chamber.
I - Defocused light source.
J - One-half light intensity.

bRates given are for second hour of run.

cInitial HONO values which give best fits to the data in detailed model calculations, or (for runs with constant [OH]) the photostationary state levels.

Table 17. Conditions and Selected Results for Indoor Teflon Chamber (ITC) NO_x-Air Irradiations

ITC Run No.	Conditions[a]	k_1[b] (min⁻¹)	RH (%)	Initial NO (ppm)	Initial NO₂ (ppm)	Average [OH] (10^6 Radicals-cm^{-3}) 0-60 min	Average [OH] >60 min[c]	Radical Flux (ppb-min⁻¹)	$-\dfrac{d[NO]}{dt}$ >60 min (ppb-min⁻¹)
382		0.45	<10	0.334	0.578	1.5	0.5	0.02	0.005
383		0.45	<10	0.354	0.068	1.1	0.8	0.04	0.03
378		0.45	~50	0.493	0.119	2.6	1.7	0.09	0.10
380		0.45	~50	0.305	0.072	1.1	1.6[d]	0.08	0.01
379	A	0.45	~50	0.098	0.222	1.8	1.3	0.16	0.12
377	B	0.45	~50	0.373	0.114	2.1	2.4	0.14	0.37
377	C	0.45	~50	0.266	0.098	–	1.6	0.11	0.31
377	C	0.45	~50	0.246	0.109	–	1.6	0.12	0.36
380	D	0.35	~50	0.312	0.076	–	1.3	0.06	0.13
380	D	0.28	~50	0.305	0.078	–	1.1	0.05	0.09
380	D	0.2	~50	0.300	0.080	–	0.6	0.03	0.06
381	E	0.2	~50	0.245	0.088	–	0.7[e]	0.04	0.05
380	D	0.1	~50	0.297	0.083	–	0.6	0.03	0.07
381		0.1	~50	0.295	0.088	0.7	0.4[f]	0.02	0.01

[a]For all runs, T = 303 K. Codes for special conditions are shown below.
A - Nonstandard initial NO and NO_2 concentrations.
B - Previously unused bag.
C - Continuation of four-hour run.
D - Continuation of run in which light intensity was incrementally reduced.
E - Continuation of run in which light intensity was incrementally increased.

[b]k_1 = NO_2 photolysis rate.

[c]Unless otherwise noted, data given are for a period of 60 minutes.

[d]Data are given for a period of 45 minutes.

[e]Data given are for 135 minutes.

[f]Data given are for 90 minutes.

[g]Data given are for 120 minutes.

Table 18. Conditions and Selected Results for Small (~100-liter volume) Teflon Bag NO_x-Air Irradiations

Run No.[a]	NO (ppm)	NO_2 (ppm)	Average [OH] (10^6 rad-cm^{-3})	Radical Source[b] (ppb-min^{-1})	$\frac{-d[NO]}{dt}$[b] (ppb-min^{-1})
4-1	0.460	0.155	5.1	0.75	2.73
4-2	0.475	0.220	3.7	0.54	1.45
4-3	0.476	0.135	3.7	0.32	1.37
4-4	0.503	0.120	4.9	0.54	1.97
4-5	0.467	0.119	4.6	0.51	1.69
5-1	0.345	0.227	1.4	0.15	0.26
5-2	0.269	0.100	1.5	0.09	0.21

[a]First number is bag number. Second number is order run was carried out with this bag.

[b]Calculated for t > 60 minutes.

Table 19. Conditions and Selected Results for Large Outdoor Teflon Chamber NO$_x$-Air Irradiations

Run No.	Bag NO$_x$	Bag History[a]	T (K)	RH (%)	k_1[b] (min^{-1})	Initial NO (ppm)	Initial NO$_2$ (ppm)	Avg. [OH] (10^6 rad-cm^{-3})	Radical Flux (ppb min^{-1})	$-\frac{d[NO]}{dt}$ (ppb min^{-1})
11	15	N	39	~50	0.41	0.485	0.124	2.1	0.19	0.86
24A[c]	16	F	41	52	0.35	0.479	0.139	1.9	0.23	0.73
24B[c]	16	F	41	48	0.35	0.461	0.138	1.9	0.22	0.10
27	17	N	36	~30	0.32	0.233	0.092	0.5	0.03	0.10
35	17	F	26	25	0.36	0.402	0.146	1.1	0.11	0.13
41	18	F	43	43	0.34	0.398	0.139	1.6[d]	0.14[d]	0.10
46	18	F	32	<10	0.34	0.368	0.149	1.0	0.10	0.10
ARB-1B[c]	18	F, NH$_3$	33	<10	0.34	0.369	0.151	1.1	0.10	0.13
47	19	N	32	<10	0.32	0.394	0.144	0.6[d]	0.06[d]	~0.0
51	19	C	33	<10	0.27	0.404	0.133	0.7[d]	0.06[d]	0.03
61	20	C	22	20	0.37	0.418	0.160	0.6	0.05	0.01

[a]Codes for bag history are as follows:

N - New bag.

C - New bag conditioned by propene-NO$_x$ irradiation, O$_3$ dark decay run, then pure air irradiation.

F - Follows aircraft or automotive fuel-NO$_x$-air irradiation carried out for another program.

NH$_3$ - NH$_3$ present in mixture (see Section II).

[b]k_1 = NO$_2$ photolysis rates calculated from the radiometric readings using the formula of Zafonte et al. (1977).

[c]Divided bag run.

[d]Data highly scattered, value given is uncertain by approximately a factor of two.
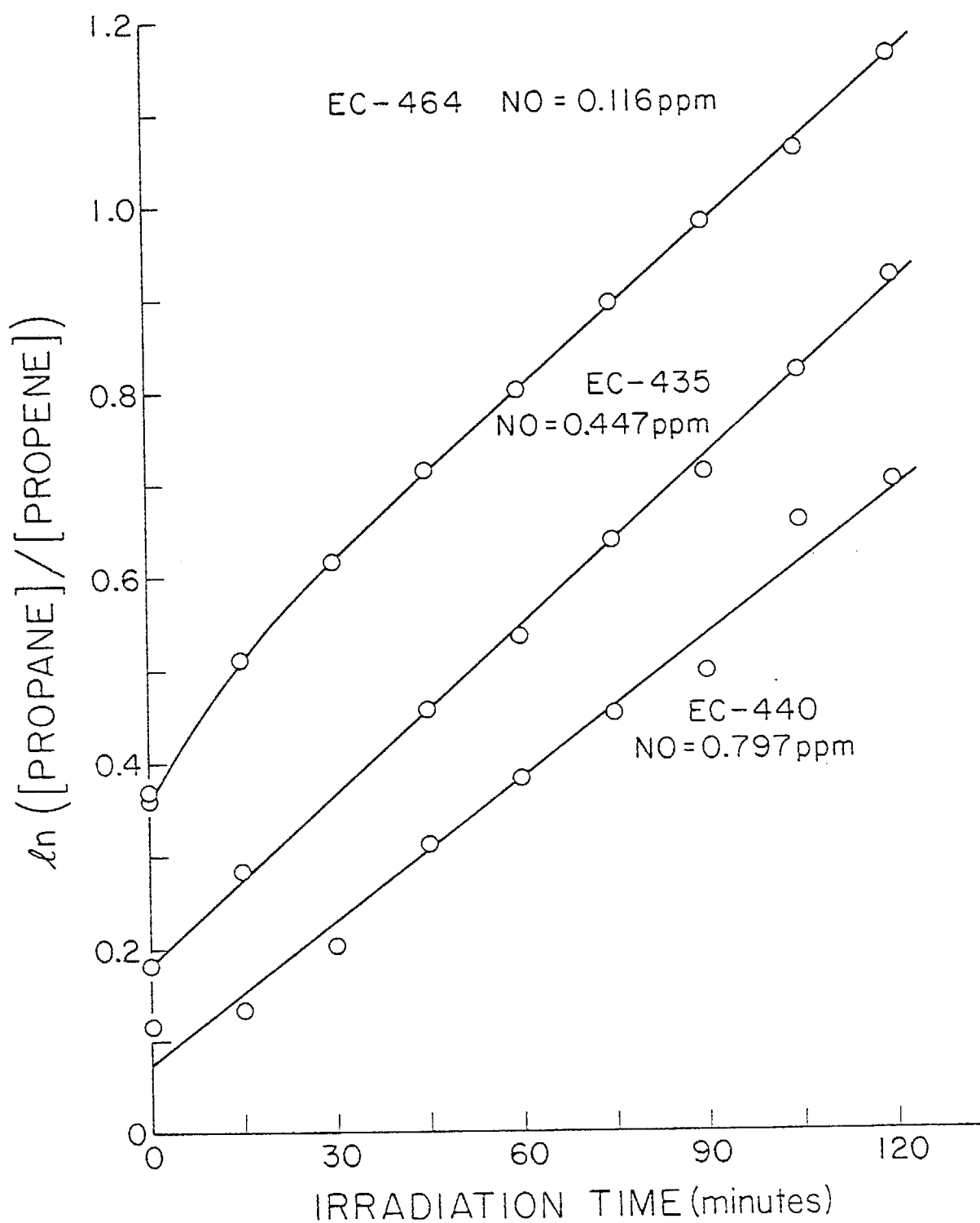
Figure 25. Plots of ln([propane]/[propene]) against irradiation time
for evacuable chamber runs with $[NO_2]_{initial} \approx 0.1$ ppm, and
varying initial NO concentrations.
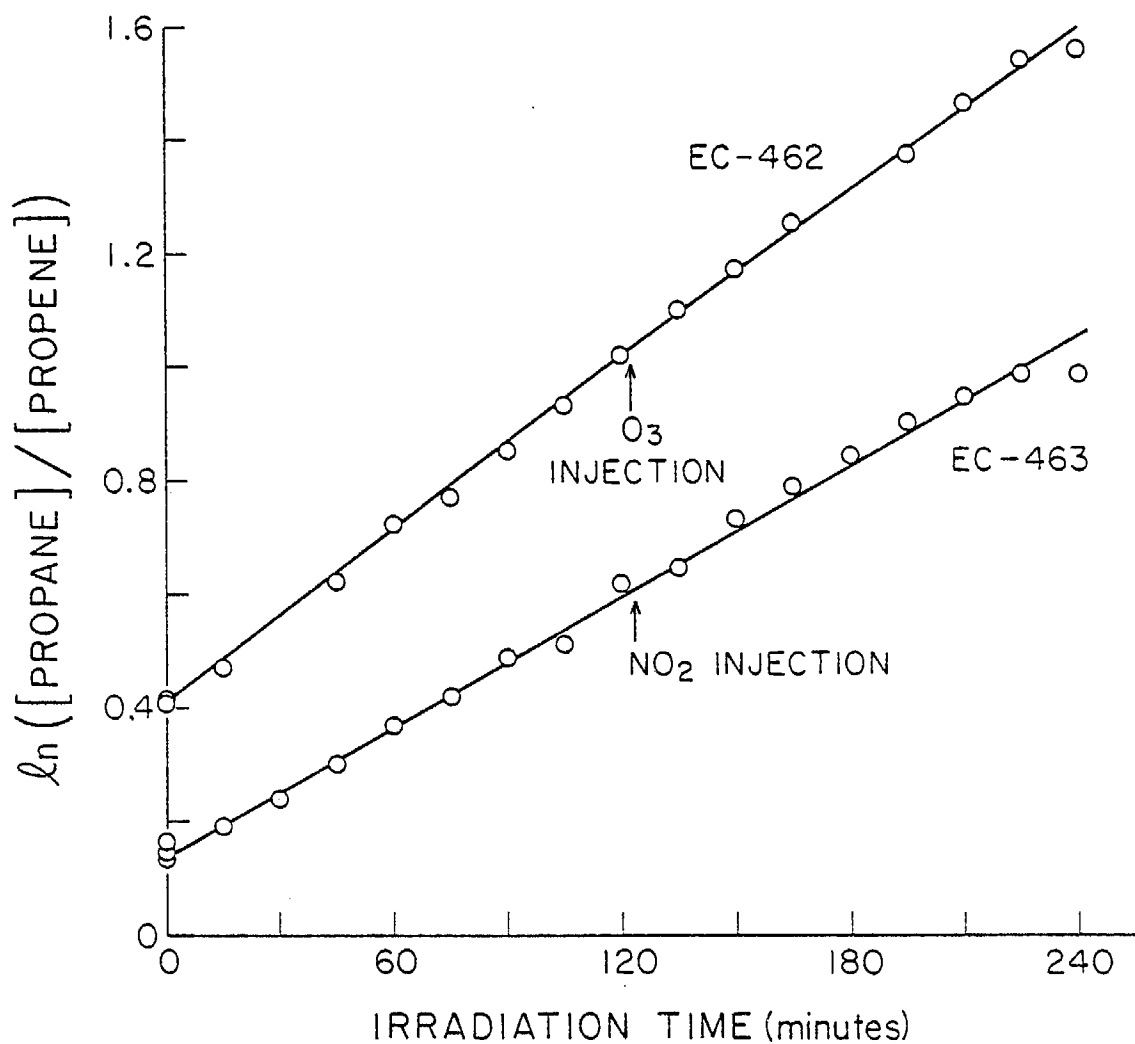
Figure 26. Plots of ln([propane]/[propene]) against irradiation time for evacuable chamber run in which O_3 or NO_2 was injected during the run.

essentially constant during the two-hour irradiations, while runs where T $\geq$ 303 K, RH > 50% or [NO]/[NO$_2$] $\leq$ 1 generally had initially higher OH radical levels which decreased to a constant value after ~30 to 60 minutes.

It can be seen from Tables 15 through 19 that a number of replicate runs were done under standard conditions [NO $\simeq$ 0.4 ppm, NO$_2$ $\simeq$ 0.1 ppm, ~50% RH (evacuable chamber and indoor Teflon chamber), < 10% RH (small bags), maximum light intensity] in the various indoor chambers. These tables show that duplicate runs give hydroxyl radical levels which are reproducible to within $\pm$ 15% in the evacuable chamber with the variability in the indoor Teflon chamber and between different small Teflon bags being somewhat greater. The variability in hydroxyl radical levels in the large outdoor chamber is considerably greater, with hydroxyl levels varying by as much as a factor of three, but these can be attributed in part to variations in temperature and light intensity characteristic of outdoor irradiations.

A comparison of average hydroxyl radical levels observed in comparable runs performed in the four chambers is shown in Table 20. Since the light intensity of the different chambers is in general different, a more direct comparison can be obtained from the hydroxyl radical concentration normalized by dividing by the light intensity (since the OH radical concentrations were observed to be proportional to light intensity, as discussed below). These values are also shown in Table 20. It can be seen that the intensity-normalized hydroxyl radical levels indeed depend significantly on the chamber employed.

It is interesting to note that the normalized OH radical levels in the Teflon chambers vary as much or more from chamber to chamber as they do with the size of the chamber. For example, the OH radical levels in the indoor Teflon chamber are slightly lower than, or (within experimental variability) essentially the same as, those observed in the oudoor chamber, despite the much larger volume of the latter. In addition, the difference between the radical levels in small Bag #5 and the large Teflon chambers is no greater than the difference between Bag #5 and Bag #4. It should be noted that the same roll of Teflon film was used to make all the FEP Teflon chambers employed in this study.

Table 20. Dependence of OH Radical Levels Observed in Comparable[a] NO_x-Air Irradiations on Chamber Employed

Chamber	k_1[b] (min^{-1})	[OH] $(10^6 \ cm^{-3})$	$[OH]/k_1$ (normalized)[c]
Small Teflon Bag #4	0.27	4.4 ± 0.7	3.1 ± 0.6
Small Teflon Bag #5	0.27	1.4	1.0
Evacuable	0.49	2.5 ± 0.2	1.0
Indoor Teflon	0.45	0.64 ± 0.1	0.3 ± 0.1
Outdoor Teflon	$\sim 0.3 \pm 0.05$[d]	0.9 ± 0.3	0.5 ± 0.2

[a]Initial [NO] $\cong$ 0.4 ppm; $[NO_2]$ $\cong$ 0.1 ppm; RH < 10%, T = 303–308 K.
[b]k_1 = NO_2 photolysis rate.
[c]Normalized to ratio observed in the evacuable chamber runs.
[d]Estimated from radiometer readings using the empirical relationship derived by Zafonte et al. (1977).

The dependence of the OH radical concentration on temperature and relative humidity for runs in the evacuable chamber, and on humidity for runs in the indoor Teflon chamber is shown in Table 21 for runs with approximately the same initial NO and NO_2 concentrations and light intensity. It can be seen that the hydroxyl radical levels increase with both temperature and humidity. The hydroxyl radical concentrations also appear to be more strongly affected by humidity in the Teflon chamber than in the evacuable chamber.

The dependence of hydroxyl radical concentrations on light intensity is shown in Figure 27, which shows plots of OH radical levels against the light intensity (as measured by k_1, the NO_2 photolysis rate) for the 5800-liter evacuable and 6000-liter indoor Teflon chamber runs in which the light intensity was varied. It can be seen that within experimental error the radical levels are proportional to light intensity.

The effect of NO levels on the results of the evacuable chamber runs is shown in Figure 25, which shows plots of ln([propane]/[propene]) against

Table 21. Dependence of OH Radical Levels Observed in Standard[a] NO_x-Air Irradiations on Temperature and Relative Humidity (RH)

Chamber	T(K)	10^{-6} x [OH] radical cm^{-3}			
		<10% RH	50% RH	80% RH	100% RH
	284	1.6	2.1		4.7
Evacuable	303	2.5	4.4	$16 \rightarrow 11$[b]	$20 \rightarrow 12$[b]
	323	5.7	$18 \rightarrow 9$[b]		$50 \rightarrow 8$[b]
Indoor Teflon	303	0.6	1.8		

[a]Initial [NO] $\cong$ 0.4 ppm; [NO_2] $\cong$ 0.1 ppm; NO_2 photolysis rate k_1 = 0.49 min^{-1} (evacuable chamber), 0.45 (indoor Teflon chamber).
[b]OH radical concentrations changed throughout the run; initial and final values given.

irradiation time for runs with a similar initial NO_2 concentration, but with initial NO concentrations varying from 0.116 to 0.797 ppm. It can be seen that the final OH radical levels (e.g., the slopes of the lines in Figure 25) are essentially unaffected by the NO concentration, but that the initial slope increases as the NO level is decreased.

The hydroxyl radical levels in the evacuable chamber runs were also not strongly affected by NO_2 levels, except in the initial stages of irradiation, where higher NO_2 levels resulted in higher initial hydroxyl levels. The relative insensitivity of the subsequent hydroxyl radical levels to NO_2 is illustrated by Figure 26 which shows the results of two runs in which NO_2 levels were increased by a factor of 2 to 2.5, either by direct injection of NO_2 or by conversion of NO to NO_2 by injection of O_3. It can be seen that the slope of the ln([propane]/[propene]) versus time plots, and thus the OH radical levels, are essentially unchanged by the sudden increase in NO_2.

In order to obtain data concerning the effect of the reactant injection technique and of other experimental conditions on the radical levels, several evacuable chamber runs were carried out using nonstandard reaction conditions.
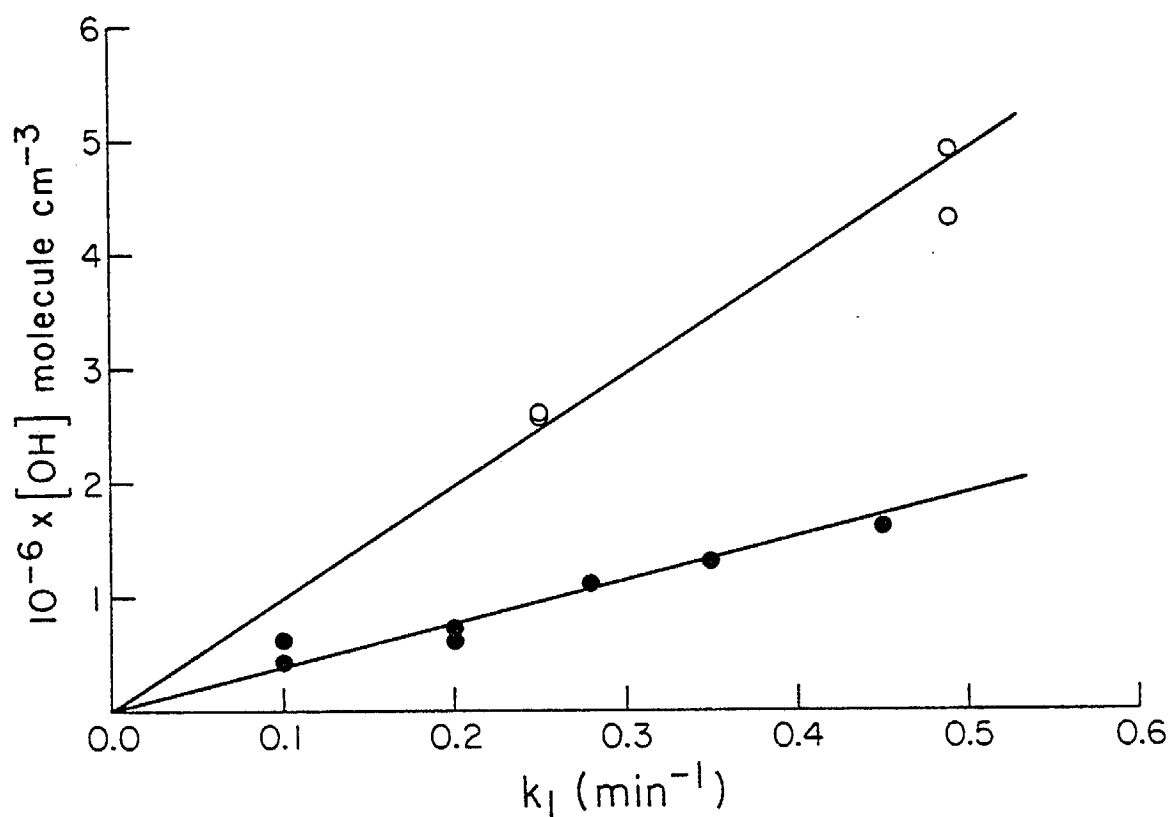
Figure 27. Dependence of average OH radical concentrations on the NO_2 photolysis rate k_1 for irradiations in which the light intensity was varied. (O – 5800-liter evacuable chamber; ● – 6000-liter all-Teflon chamber).

The results of these are briefly summarized below (see also Table 16).

• One run was carried out in which NO and NO_2 were injected using the syringe injection technique employed on the other chambers, instead of the vacuum technique (see Experimental section above). The results of this run were essentially the same as for the standard runs.

• One run was conducted in which NO_2 was prepared by reacting NO with O_3 in the chamber, rather than by reacting O_2 with NO at high concentrations prior to injection into the chamber, which is the usual procedure. The resulting hydroxyl radical concentration was 35-40% lower than the average of the standard runs; this deviation is somewhat greater than the observed $\pm$ ~15% variability of the standard runs.

• One run was carried out by introducing NO into the chamber ~27 hours prior to the start of the irradiation, with NO_2 being formed to approximately its usual pre-irradiation value by the NO dark oxidation reaction. In that run, the initial hydroxyl radical level was approximately 2.5 times higher than in the standard runs, with the hydroxyl radical concentrations leveling off to values ~25% higher than those in the standard runs. (Hydroxyl radicals levels in the standard runs were generally reproduceable to $\pm$ 15%).

• In order to assess the possible role of surface photochemistry, one run was carried out under otherwise standard conditions with the solar simulator beam defocussed so that more light would impinge on the Teflon surface. The hydroxyl radical levels observed in both portions of this run (i.e., at both full- and half-light intensity) were within the range of those observed in the full- and half-light intensity standard runs.

• One low humidity run was carried out following an evacuated bakeout of the chamber at 363 K. In that run the hydroxyl radical levels were initially ~1.8 times higher than in the other low humidity runs, though they declined, being ~28% higher by the end of the run. In contrast, the hydroxyl radical levels in the other low humidity runs were constant during the duration of the irradiations.

Discussion. In irradiated NO_x-air mixtures, the major gas phase reactions (Hampson and Garvin 1978, Carter et al. 1979a, Atkinson et al. 1980, Baulch et al. 1980, Atkinson and Lloyd 1980) are as follows:

$$NO_2 + h\nu \ (\lambda \geq 295 \ nm) \rightarrow NO + O(^3P) \tag{1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

$$O(^3P) + NO_2 \rightarrow NO + O_2 \tag{4}$$

$$O(^3P) + NO_2 \overset{M}{\rightarrow} NO_3 \tag{5}$$

$$NO + NO + O_2 \rightarrow 2 \ NO_2 \tag{6}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{7}$$

$$NO_3 + NO \rightarrow 2 \ NO_2 \tag{8}$$

$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2 \tag{9}$$

$$NO_3 + NO_2 \overset{M}{\rightarrow} N_2O_5 \tag{10}$$

$$N_2O_5 \overset{M}{\rightarrow} NO_2 + O_3 \tag{11}$$

$$NO_3 + h\nu \rightarrow NO + O_2 \tag{12}$$

$$NO_3 + h\nu \rightarrow NO_2 + O(^3P) \tag{13}$$

$$O_3 + h\nu \rightarrow O_2 + O(^3P) \tag{14}$$

$$O_3 + h\nu \ (\lambda \leq 310 \ nm) \rightarrow O_2(^1\Delta g) + O(^1D) \tag{15}$$

$$O(^1D) + M(M = air) \rightarrow O(^3P) + M \tag{16}$$

$$O(^1D) + H_2O \rightarrow 2 \ OH \tag{17}$$

$$OH + NO \overset{M}{\rightarrow} HONO \tag{18}$$

$$HONO + h\nu \rightarrow OH + NO \tag{19}$$

$$OH + NO_2 \overset{M}{\rightarrow} HNO_3 \tag{20}$$
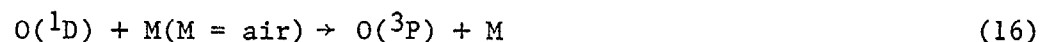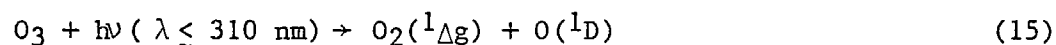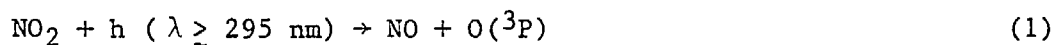
Under the conditions of the experiments described here, where significant concentrations of NO are always present, the O_3 concentrations are sufficiently low that reactions (7)-(17) are of minor importance. In particular, the OH radical input rate calculated from the above mechanism for

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conditions of a typical evacuable chamber run where $[NO] = [NO_2]$ is $\sim 4 \times 10^{-6}$ ppm^{-1} min^{-1}, which gives rise to predicted OH radical levels one to two orders of magnitude lower than those actually observed.

The major additional reactions occurring when propene and propane are included in the reaction mixture can be represented overall as follows (Carter et al. 1979a, Atkinson and Lloyd 1980):

$$\text{OH + propene} \xrightarrow[\substack{2\,O_2 \\ \\ 2\,NO_2}]{2\,NO} \text{HCHO + CH}_3\text{CHO + OH} \qquad (21)$$

and

$$\text{OH + propane} \xrightarrow[\substack{2\,O_2 \\ \\ 2\,NO_2}]{2\,NO} \text{H}_2\text{O + CH}_3\text{COCH}_3 \text{ + OH} \qquad (22)$$
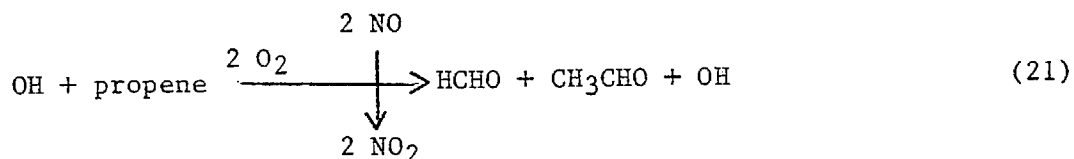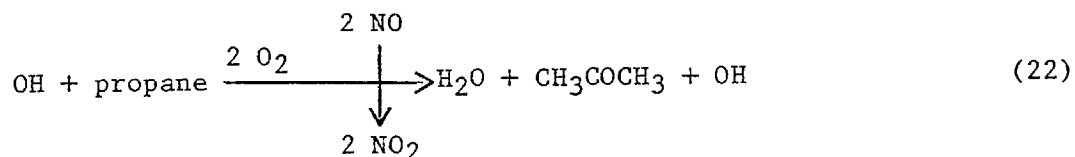
Under the conditions employed in these runs, reaction of propene with O_3, $O(^3P)$, NO_3, etc., are negligible; in particular, reaction with O_3 was always < 10%, and generally ~1%, of the total loss processes for propene (Carter et al. 1979a, Atkinson and Lloyd 1980). Reaction of propene and propane with OH radicals thus results in no net production of radicals, but causes the conversion of two molecules of NO to NO_2. At the reactant levels employed in these runs, the rate of this conversion is minor, being generally less than the conversion caused by the CO impurity concentrations observed (0.5 to 4 ppm).

$$\text{OH + CO} \xrightarrow[NO_2]{\substack{O_2 \\ \\ NO}} \text{OH + CO}_2$$
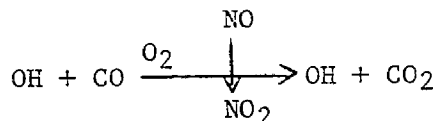
Photodissociation of the oxygenated propene and propane products can lead to radical production, but at the reactant levels employed in these runs, these radical sources are also minor (Carter et al. 1979a, Atkinson and Lloyd 1980).

The hydroxyl radical levels observed in all the runs reported here were significantly higher than expected from the homogeneous reactions

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discussed above. This is illustrated in Figures 28 and 29, which show hydroxyl radical concentration-time profiles derived from the data of a representative standard evacuable chamber run (Figure 28), and from a representative high initial NO_2 concentration run (Figure 29), and compares them with results of model calculations (curve A) using only the known gas phase chemistry (Carter et al. 1979a, Atkinson et al. 1980, Atkinson and Lloyd 1980). (It should be noted that the largest single radical source in these calculations was formaldehyde photolysis, and the calculations used the observed initial formaldehyde levels of 20 ppb, and 6 ppb, respectively, which are taken to be upper limits for [HCHO] given the uncertainties associated with the chromatropic acid method.) It can be clearly seen that the known radical sources are at least an order of magnitude too low to account for the observed radical levels in these runs.

As discussed in the introduction to this section, previous computer modeling studies have accounted for this excess radical source either by assuming initially present nitrous acid, whose rapid photolysis (reaction 19) can produce radicals at a significant rate even when only low levels of HONO are present, or by assuming a constant radical flux whose source is unspecified. Figures 28 and 29 show the results of model calculations assuming (B) only initially present HONO (at levels adjusted to fit the initial hydroxyl radical concentrations) and of calculations (C) assuming a constant radical flux at rates adjusted to fit the final OH radical levels, together with calculations (D) assuming a combination of both. It can be seen that assuming only initial HONO greatly underpredicts radical levels after the initial ~15 minutes of the run, and initial HONO can be, at best, only a minor contributor to the observed radical source after the first ~30 minutes of irradiation. On the other hand, using only a constant radical flux in the calculation results in underprediction of initial OH radical levels, especially in the high $[NO_2]/[NO]$ runs, and best fits to the data are obtained if some contribution due to initial HONO is assumed. However, in terms of the overall input of radicals during a chamber irradiation (typically $\geq$ 6 hours for smog simulation runs) the constant radical flux is by far the more important factor.
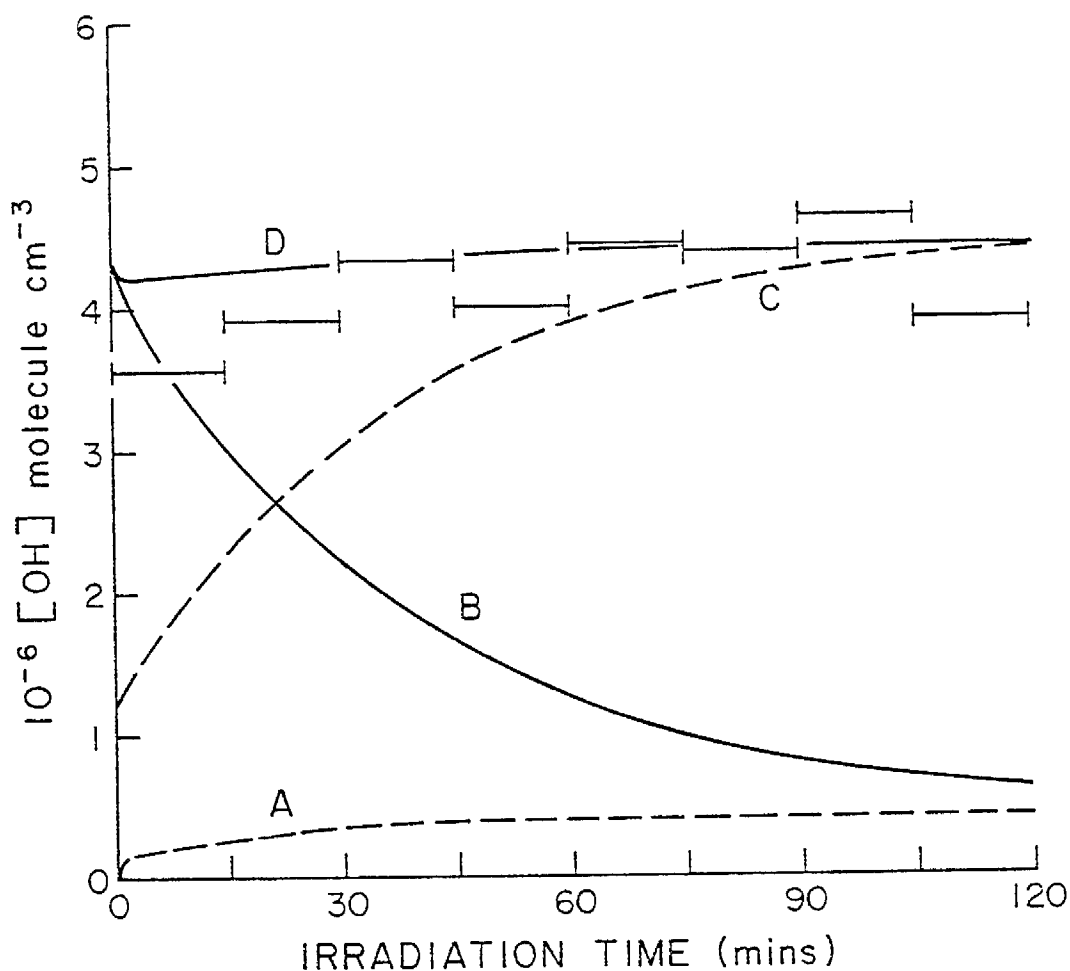
Figure 28. Hydroxyl radical concentrations as a function of irradiation time. |——| experimental data for EC-457; $[NO]_{initial}$ = 0.499 ppm, $[NO_2]_{initial}$ = 0.115 ppm; $[propane]_{initial}$ = 0.013 ppm, $[propene]_{initial}$ = 0.010 ppm; $[HCHO]_{initial}$ ≈ 0.020 ppm, T = 303 K, RH = 50%, NO_2 photolysis rate constant k_1 = 0.49 min^{-1}; A - model calculations with the homogeneous gas phase chemistry; B - model calculations with $[HONO]_{initial}$ = 0.010 ppm; C - model calculations with a constant OH radical flux of 0.245 ppb min^{-1}; D - model calculations with $[HONO]_{initial}$ = 0.010 ppm and a constant OH radical flux of 0.245 ppb min^{-1}.

Figure 29. Hydroxyl radical concentrations as a function of
irradiation time. |———| experimental data for EC-
442; A - model calculations with the homogeneous gas
phase chemistry; B - model calculations with $[HONO]_{initial}$
= 0.050 ppm; C - model calculations with a constant OH
radical flux of 0.61 ppb min^{-1}; D - model calculations
with $[HONO]_{initial}$ = 0.050 ppm and a constant OH radical
flux of 0.61 ppb min^{-1}.

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The radical flux required to fit the data for a given run can be estimated (without the necessity to carry out detailed model calculations) from the fact that radical initiation and radical termination must balance. Since the only significant radical termination processes in this system are the reactions of OH radicals with NO and NO$_2$ (reactions 18 and 20), and since the only major known radical initiation process is HONO photolysis (reaction 19), then

$$R_u + k_{19}[HONO] = k_{18}[OH][NO] + k_{20}[OH][NO_2]$$

where R$_u$ is radical initiation from all sources other than HONO photolysis. Since reactions (18) and (19) are the major reactions affecting HONO levels, the above can be rearranged to yield

$$R_u = \frac{d[HONO]}{dt} + k_{20}[OH][NO_2]$$

Furthermore, since the photolytic half-life of HONO in these experiments is $\leq$ 15 minutes, HONO is in photostationary state after the first hour. Therefore, the radical initiation rates for t > 60 minutes in these photolyses can be estimated from the equation:

$$R_u \ (t \geq 60 \ min) \cong k_{20}[OH]_{avg}[NO_2]_{avg}$$

where k$_{20}$ is accurately known (Hampson and Garvin 1978, Atkinson and Lloyd 1980) and [OH]$_{avg}$ and [NO$_2$]$_{avg}$ are experimentally determined. It should be noted that, in general, the OH radical levels were approximately constant after the first hour.

The radical input rates estimated in this way for the second and subsequent hours of the various runs are summarized in Tables 16 through 19 for the various chambers. It should be noted that these rates are one to three orders of magnitude greater than the maximum rates of the known homogeneous radical initiation processes such as O$_3$ or oxygenate photolysis (see above), and thus these values of R$_u$ can be considered to measure the radical flux from unknown sources. Furthermore, in runs with similar reactant levels, and thus similar values of [NO$_2$]$_{avg}$, the calculated radical flux is approximately proportional to [OH]. Thus, the dependence of [OH] on temperature, humidity (see Table 21), light intensity (Figure

27), and on the chamber employed (Table 20) reflect directly the corresponding dependence of the radical flux on these parameters (i.e., the unknown radical flux increases significantly with temperature and humidity, appears to be proportional to light intensity, and is different when different chambers are employed).

Although the hydroxyl radical levels, and thus the radical flux, were observed to be unaffected by NO levels, the radical flux is significantly affected by NO_2 levels. In particular, if the addition of NO_2 to the reaction mixture does not change the OH radical levels (see Figure 26), despite the fact that reaction with NO_2 is the major radical sink, then the radical flux must be approximately proportional to $[NO_2]$.

The dependence of the calculated radical flux on second-hour average NO_2 levels for the ~50% RH, 303 K evacuable chamber runs is shown in Figure 30 (data for the two irradiations carried out at lower light intensity (EC-457 and 458) are included, the observed radical fluxes being corrected to be consistent with a value of $k_1 = 0.49$ min^{-1}). The data are fit by the regression line

$$R_u \text{ (ppb min}^{-1}) = k_1[(0.30 \pm 0.06) + (2.9 \pm 0.3)[NO_2]_{avg}]$$

(where the NO_2 concentration is in ppm), as shown in Figure 30. It can be seen that although the radical flux increases with $[NO_2]$, the intercept appears to be significantly greater than zero, suggesting that the radical source may be non-negligible, even in the absence of NO_2.

Insufficient data are available to determine quantitatively the dependence of the radical source on $[NO_2]$ in the other chambers employed or at the high and low temperatures in the evacuable chamber, but they do appear to be positively correlated. The one exception appears to be the T = 323 K, 50% RH runs in the evacuable chamber, where the radical source appears to be independent of $[NO_2]$ (compare run EC-451 with runs 447 and 448 in Table 16). On the other hand, the two T = 284 K, ~50% RH runs in the evacuable chamber (EC-452 and 455, Table 16) can be fit within experimental error by a line with zero intercept and the same slope as derived from the R_u vs. $[NO_2]_{avg}$ regression for T = 303 K.

In principle, it may be possible to obtain some indication as to the nature of the radical source from the rate of NO consumption observed in
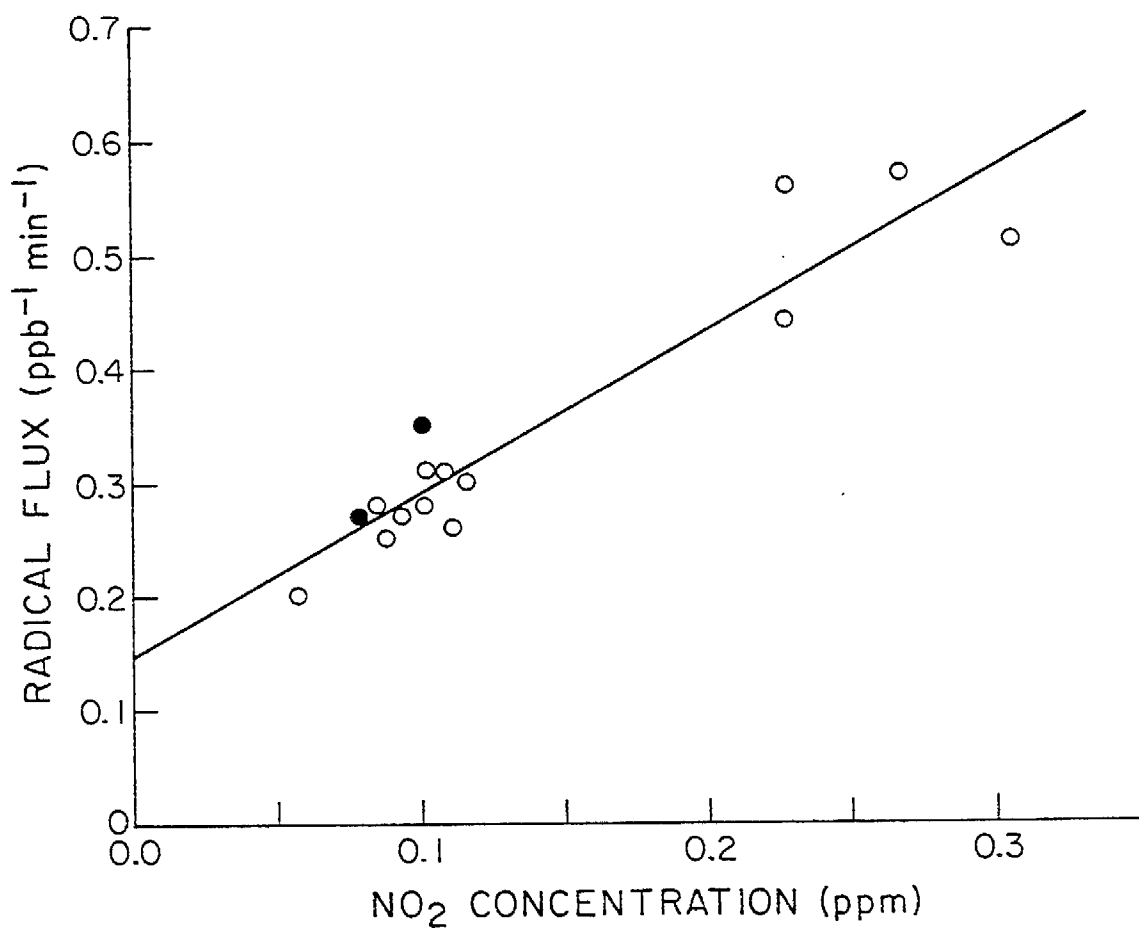
Figure 30. Dependence of estimated radical flux on the average NO_2 concentration for $t > 60$ mins in standard evacuable chamber irradiations at 303 K and 50% RH. (O – data at $k_1 = 0.49$ min^{-1}; ● – data at $k_1 = 0.25$ min^{-1}, corrected to $k_1 = 0.49$ min^{-1}; see text).

these runs. NO consumption is caused by dilution, by the reactions of peroxy radicals (formed in the photooxidations of propene, propane, CO, HCHO and other organic contaminants) with NO, by the dark oxidation of NO (reaction 6), and by the formation of NO_3 from the reaction of $O(^3P)$ with NO_2 (reaction 5, followed by reaction 8). This is balanced in part by NO_2 to NO conversion resulting from the reaction of $O(^3P)$ atoms with NO_2 (reaction 4). If the unknown radical flux is due to formation of HO_2, as postulated by Hendry et al. (1978), then it would cause additional NO consumption due to the reaction of HO_2 with NO. If the radical flux is due to the formation of OH, as initially postulated by Carter et al. (1979a), then it would have no effect on NO consumption. If, however, the radical flux is due to a process such as, for example

$$NO_2 + wall.H_2O \rightarrow wall.OH + HONO$$
$$HONO + h\nu \rightarrow OH + NO$$
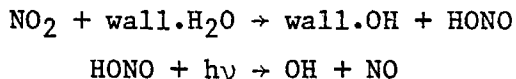
then the radical source would reduce the rate of NO consumption.

The observed NO conversion rates for the second hour of the evacuable chamber runs are summarized in Table 16, along with rates calculated from the known processes (Carter et al. 1979a, Atkinson and Lloyd 1980). It should be noted that if there are undetected organic contaminants, the conversion rate would be underpredicted, and thus the calculated values should be considered to be lower limits. In general, except for the high temperature, humidified runs, where probable contamination effects cause the observed conversion rates to be consistently high, it can be seen that the observed conversion rates are either approximately equal to or lower than the calculated values. Since the NO loss rate is not consistently higher than predicted, the radical source is unlikely to involve formation of HO_2 or any other radical which consumes NO, and in fact, the data appear to be most consistent with the assumption that some net NO formation may be involved in the radical flux.

Finally, as mentioned above, the initial hydroxyl radical levels suggest that HONO may be initially present. In the runs with constant OH radical levels, the initially present HONO must be approximately equal to the photostationary state value; for the other runs, it is most reliably obtained by adjusting the initial HONO and the radical flux to fit the data

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in detailed model calculations. Table 16 summarizes the initial HONO levels which are necessary to fit the observed OH radical concentrations for selected evacuable chamber runs. It can be seen that the apparent initial HONO required to fit the data is quite variable, but in general it increases with temperature, humidity and NO_2, with initial NO_2 having the largest effect, at least for $T \leq 303$ K. Surprisingly, it also appears that high levels of initial NO tend to suppress the apparent initial HONO (compare run EC-434 with EC-445). This then rules out the reaction

$$NO + NO_2 + H_2O \rightarrow 2 \ HONO$$
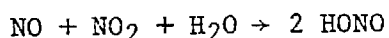
in the chamber as being the source of the initial HONO.

Conclusions. The results of the experiments reported here show conclusively that radical input from unknown sources is an important process in smog chamber systems, and that, in terms of the total number of radicals produced, initial HONO is at most a minor contributor to this process. Thus it is clear that photochemical smog models validated against chamber data assuming only initial HONO as the radical source must be re-evaluated. However, it is also clear that assuming only a constant radical flux during an irradiation is also an oversimplification, particularly in view of the fact that it generally underpredicts radical levels in the initial stages of the irradiation, and that it does not take into account the dependence of apparent radical flux on NO_2 levels, which in general varies during typical smog chamber irradiations.

Radical input from unknown sources is strongly influenced by both temperature and relative humidity. This fact should be taken into account when using smog chamber data to assess the effects of these parameters on photochemical smog formation. In particular, the apparent strong dependence of smog formation potential on temperature reported by us previously (Carter et al. 1979b) may be wholly or partially a result of this radical source effect.

Radical input from unknown sources is also highly dependent on the chamber employed. Thus, the radical source must be considered to be another chamber effect which (like O_3 wall destruction) must be measured periodically by appropriate control experiments in order for the data obtained to be adequately characterized. NO_x-air irradiations such as

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those described here appear to be useful in measuring this effect, and we strongly recommend that all future experimental protocols involving smog chamber irradiations include NO_x-air irradiations among the associated characterizations and control experiments.

Although the results of the experiments reported here are not adequate to establish the exact mechanism causing this effect, it has given us some indications as to its nature and allowed a number of possibilities to be ruled out. As mentioned previously, HONO formed during NO_x injection cannot be the only radical source, though the results of some experiments reported here suggest that it may contribute in the initial stages of the irradiations. It can also not be due to HONO formation from the reaction

$$NO + NO_2 + H_2O \rightarrow 2 \text{ HONO}$$
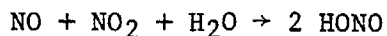
since NO seems to have no effect on the radical flux, and indeed appears to inhibit initial HONO levels.

The fact that the radical flux appears to be proportional to light intensity means that contaminant offgassing cannot be a rate determining step. In addition, the facts that (a) the radical flux depends on the chamber employed, (b) that previously unused Teflon chambers have a significant radical flux, (c) that the radical flux is higher in the evacuable chamber after it is "pumped and baked" than it is following standard evacuable chamber runs, and (d) that the flux depends on humidity, suggests that this effect is due to a heterogeneous reaction and is not a result of contamination. This heterogeneous reaction appears to involve NO_2 and H_2O and must involve some sort of rapid equilibrium in order to be consistent with the results reported here.

It is clear that additional experiments are required to further characterize the nature of this radical source and to determine the role, if any, of initially present HONO.

V. EXPLORATORY LONG-PATH FT-IR STUDIES OF THE ATMOSPHERIC REACTIONS OF MODEL PESTICIDE COMPOUNDS

Increasing attention is being focused on the environmental hazards posed by pesticide materials and their transformation products in the entire ecosystem, i.e., in soil, water and the atmosphere. The yearly application of pesticide chemicals in the United States (Lewis and Lee 1976) presently exceeds one billion pounds and estimates of pesticide use in California amount to as much as 20% of national use. Table 22 provides recent usage levels in California along with data on the volatility of the major pesticidal compounds in use.

Recently, the California Air Resources Board has been concerned with reactive organic gas emissions from pesticide formulations and their possible contribution to oxidant formation in the California central valleys (Weins 1977). Posing the most immediate and serious health hazard, however, is the exposure of humans to specific active pesticide ingredients and their possible photodegradation products. Thus, numerous outbreaks of poisoning among orchard workers following use of parathion have been reported (Spear et al. 1975, Kleinman 1963), often as a result of exposures in the field several days after application. Parathion (I), which is one of the most toxic pesticides, is known to yield the even more highly toxic paraoxon (II) on irradiation or exposure to ozone. Paraoxon has been suggested as contributing to the toxicity levels encountered in these poisoning cases.

Although photodegradation is an effective pathway for removal of many pesticides in air and other media, sunlight irradiation has been known to promote "toxic synthesis" leading to products which are more toxic and potentially more persistent in the environment than the parent compounds. Examples are photodieldrin (IV) (Rosen et al. 1966), the photochemical product of dieldrin (III) and the oxon analogs of the parent organophosphorus compounds (Crosby 1972). On irradiation in solution, carbaryl (V) undergoes an elimination reaction to generate 1-naphthol, other phenols and the highly toxic and volatile methyl isocyanate (Crosby 1972, Crosby et al.

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OC_2H_5

$C_2H_5O-P=S$

O

I

$\xrightarrow[\text{surface, air}]{h\nu}$

OC_2H_5

$C_2H_5O-P=O$

O

NO_2

II

$+$

SC_2H_5

$C_2H_5O-P=O$

O

NO_2

$+$

OH

NO_2

NO_2
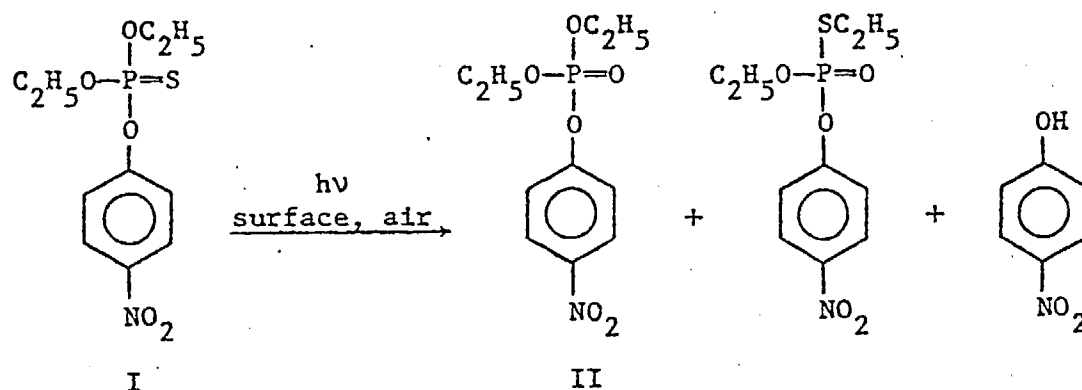
1965). Thioethers such as demeton (a mixture of VI and VII) form sulfoxides (VIII and IX) that are often more powerful inhibitors of cholinesterases than are the parent compounds (Cook 1954, Fukuto et al. 1955).

It is obvious that knowledge of the phototransformation products of pesticides in the environment are essential to the safe use of existing chemicals and the introduction of new ones. While numerous studies on the photochemistry of various pesticides have been published, the majority of the experiments have been conducted in aqueous solutions and in other organic solvents (Rosen 1972, Glofelty 1978). The gas phase photooxidation studies conducted have employed aritifical irradiation and none have included measures of photochemical reaction rates (Moilanen et al. 1976).

Since the atmosphere is a possible route for significant pesticide transport and distribution, it is important that studies include not only the identification of transformation (photooxidation) products but provide equally important kinetic information on the reactions of pesticidal materials with the atmospherically important reactive species ozone (O_3) and hydroxyl (OH) radicals. Such data are essential in providing estimates of atmospheric lifetimes both in the "clean" troposphere and in urban environments.

This exploratory work deals with the reactions of O_3 (in the dark) and the OH radical (via photooxidation in the presence of oxides of nitrogen) under simulated atmospheric conditions with three model pesticide compounds: phenyl N-methylcarbamate, trimethylphosphate and trans-1,3-dichloropropene. The first two compounds are representative of carbamates

III → (hν) → **IV**

V + (hν) → naphthalen-1-ol + CH_3NCO

$$\underset{\text{VI}}{\underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{S}{=}\!\!-OC_2H_4SC_2H_5} \xrightarrow[\text{air}]{h\nu} \underset{\text{VIII}}{\underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{S}{=}\!\!-OC_2H_4\overset{O}{\underset{\uparrow}{S}}C_2H_5} \longrightarrow \underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{S}{=}\!\!-OC_2H_4\overset{O}{\underset{\underset{O}{\uparrow}}{S}}C_2H_5$$

$$\underset{\text{VII}}{\underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{O}{=}\!\!-SC_2H_4SC_2H_5} \xrightarrow[\text{air}]{h\nu} \underset{\text{IX}}{\underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{O}{=}\!\!-SC_2H_4\overset{O}{\underset{\uparrow}{S}}C_2H_5} \longrightarrow \underset{C_2H_5O}{\overset{C_2H_5O}{>}}P\overset{O}{=}\!\!-SC_2H_4\overset{O}{\underset{\underset{O}{\uparrow}}{S}}C_2H_5$$
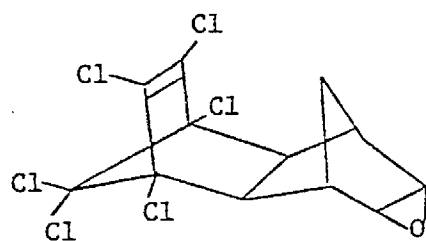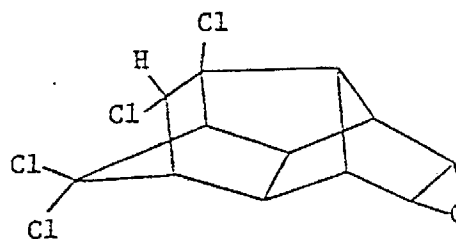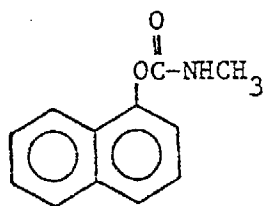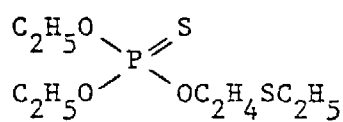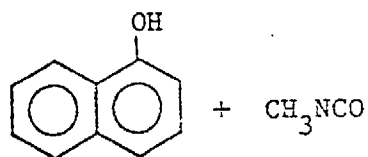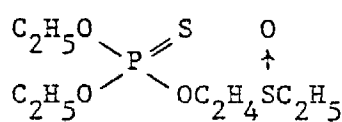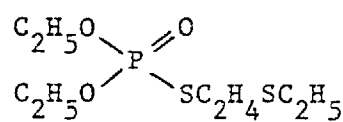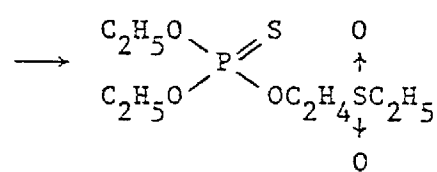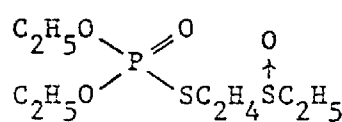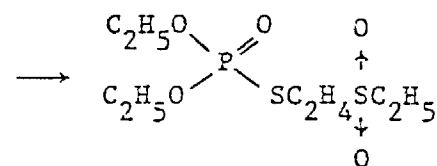
Table 22. California Usage and Vapor Pressure Data for Selected Pesticides

PESTICIDE	1975 USAGE IN CALIFORNIA (thousand pounds)*	VAPOR PRESSURE (mm Hg)	APPROX. SATURATION CONC (ppm) $25^{\circ}C$
Synthetics			
Methyl bromide	7,164	High (b.p. $4.5^{\circ}C$)	
D-D mixture	3,177	High (p.p. $90-115^{\circ}C$)	
Chloropicrin	1,902	23.8 @ $25^{\circ}C$	31300
DNBP	1,742	(m.p. $38-42^{\circ}C$)	
Telone	1,366	High (b.p. $104^{\circ}C$)	
Toxaphene	1,004	0.2-0.4 @ $25^{\circ}C$	260 - 520
Carbaryl	1,002	$\sim 5 \times 10^{-3}$ @ $26^{\circ}C$	6.5
Ordram	962	8.75×10^{-3} @ $25^{\circ}C$	11.5
Parathion	913	3.78×10^{-5} @ $20^{\circ}C$	0.05
Methomyl	854	5×10^{-5} @ $25^{\circ}C$	0.006
2,4-D, Propyleneglycol-butylether ester	805	Probably $<10^{-3}$ @ $25^{\circ}C$	<1.3
Chlordane	697	10^{-7} @ $25^{\circ}C$	.013
Omite	642	?	
DBCP and related compounds	634	0.8 @ $21^{\circ}C$	1050
Difolatan	565	Negligible (m.p. $160-161^{\circ}C$)	
Phorate	548	8.4×10^{-4} @ $25^{\circ}C$	1.1
Kelthane	509	(m.p. $78.5-79.5^{\circ}C$)	
Methyl parathion	494	9.7×10^{-6} @ $20^{\circ}C$	0.013
Dimethoate	474	8.5×10^{-6} @ $25^{\circ}C$	0.011
Endosulfan	471	No measurable v.p. at $75^{\circ}C$	
Malathion	455	4×10^{-5} @ $30^{\circ}C$	0.053
DEF	427	(b.p. $150^{\circ}C$ @ 0.3 torr)	
2,4-D Dimethylamine salt	427	(m.p. $85-87^{\circ}C$)	
Disyston	433	1.8×10^{-4} @ $20^{\circ}C$	0.24
Ethylene dibromide	407	11.0 @ $25^{\circ}C$	14500
Paraquat dichloride	393	Negligible (dec. $\sim 300^{\circ}C$)	
MCPA, Dimethamine salt	383	Probably negligible	
Guthion	316	3.8×10^{-4} @ $20^{\circ}C$	0.5
Diazinon	309	1.4×10^{-4} @ $20^{\circ}C$	0.18
Dacthal	308	~ 0.5 @ $40^{\circ}C$	600

*Compiled from Pesticide User Report system (ARB Report No. PD-77-002, December 1977).

and organophosphates, respectively, classes of compounds which have increasingly replaced organochlorine pesticides. While phenyl N-methyl-carbamate $[C_6H_5\overset{\overset{O}{\|}}{O}CNHCH_3]$ is not known to be pesticidal, it may be considered structurally as the parent of all ring-substituted carbamates, the majority of which have pesticidal properties. Trimethylphosphate $[(CH_3O)_3P=O]$ is the simplest member of the orthophosphate esters and, although not itself used as a pesticide, it is known to be toxic, has mutagenic properties and is of concern as an impurity in commercial organophosphate preparations. The third compound chosen for study was 1,3-dichloropropene (cis and trans isomers) which is used alone as a soil fumigant but is even more widely employed in a 2:1 mixture with 1,3-dichloropropane (known as D-D mixture, see Table 22) for control of nematodes.

A study of methylbromide, CH_3Br, was also considered but given the rate constant for the reaction of OH radical with CH_3Br ($k = 4 \times 10^{-4}$ cm^{-3} $molecule^{-1}$ sec^{-1} at room temperature [Atkinson et al. 1979]), its photo-oxidation reactions would be much too slow to be studied with our available experimental techniques.

Experimental

Chamber Construction. The outdoor chamber, multiple-reflection optics, and FT-IR spectrometer employed in this study are illustrated in Figure 31. The reaction chamber is essentially a large Teflon bag of triangular cross-section held semi-rigidly by a framework of steel pipes. The 50 μm (2 mil) thick FEP Teflon wall provides excellent transmission (> 98%) of solar actinic radiation. Depending on the degree of inflation, the chamber's volume ranges from ~30,000 to 33,000 liters as measured by injection of a calibration gas. Experiments are usually conducted with an initial slight overpressure (corresponding to a volume of ~32,000 liters) in the chamber such that, even with a small degree of leakage, concentrations remain essentially unaffected. The outer frame supports a two-section white tarpaulin cover which can readily be removed to expose the chamber to solar radiation. This tarpaulin transmits ≤ 0.1% of noon sunlight (as verified with a radiometer) and is therefore employed also as an opaque cover for dark experiments.
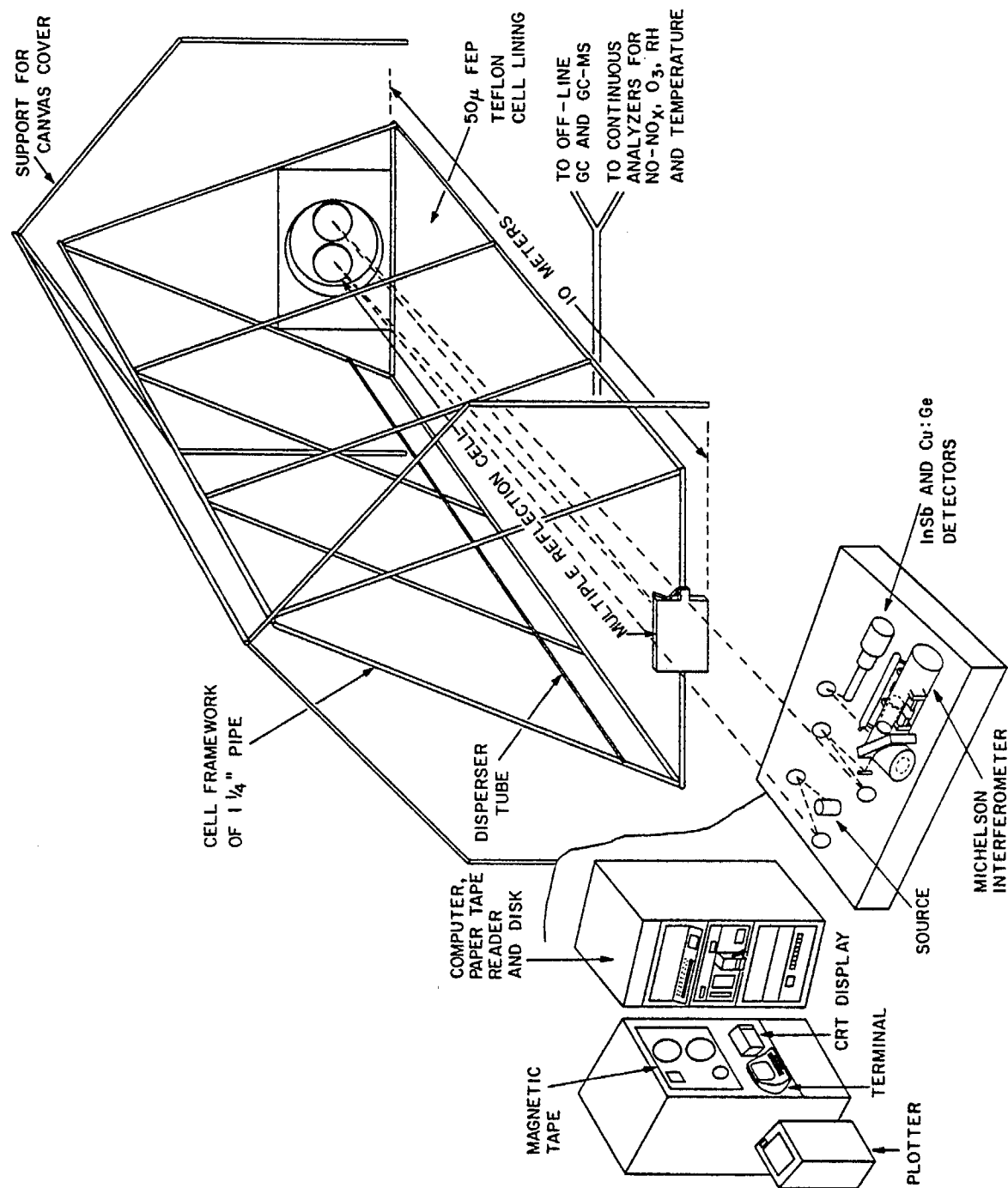
Figure 31.   FT-IR spectrometer and 30,000-liter outdoor chamber facility with in situ multiple reflection optics.

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Provisions for sample injection and gas sampling consist of several glass tubes with sealed fittings situated in the middle section of the chamber, and a Teflon disperser tube which runs the length of the cell. A Teflon-coated panel making up each of the chamber's end sections attaches to the mirror assembly by a cylindrical tube of Teflon film, thereby reducing to a minimum the vibration transmitted by the chamber to the cell optics. The end panels also provide the attachments for the mixing fans and the purge inlet and exhaust ports.

Long-Path Optics. The optical system consists of two 30 cm diamter collecting mirrors and a 15 cm x 25 cm rectangular mirror at the in-focus end with a common radius of curvature of 10 meters. The in-focus mirror is modified with the addition of a corner reflector which returns the output beam for additional sets of reflections, thereby doubling the number of passes obtainable with the conventional White design. Pathlengths in excess of 1 km can be achieved with the use of high-reflectivity ($\geq$ 99.0%) fresh gold coating on the mirrors. The kinematic mounts employed in this system have provided satisfactory alignment stability during actual operation over ambient temperature variations of up to $\pm$15 K.

FT-IR Spectrometer. A rapid-scan Midac interferometer with a maximum resolution capability of 0.06 cm^{-1} is interfaced to the multiple-reflection optics. It is equipped with a dual element, liquid N_2-cooled HgCdTe and InSb detector. The interferometer and data system are housed in a 3.6 m x 3.6 m air conditioned building immediately adjacent to the outdoor chamber. Data collection and processing are performed with a Computer Automation LSI-2/20 minicomputer with 32K words and a special FFT processor. System peripherals include a 2.5 M word dual-disk drive, raster plotter, line printer, oscilloscope display, CRT terminal and magnetic tape unit.

Materials. Trimethylphosphate (stated purity 97%, Aldrich Chemical Company) and trans-1,3-dichloropropene (Pfaltz and Bauer, IR spectrum verified) were used without further purification.

Phenyl N-methylcarbamate was prepared from the reaction of phenol and methylisocyanate according to the procedure of Addison et al. (1975). The recrystallized product had a melting point of 82°C compared to the reported value of 75°C (Addison et al. 1975); however, the UV spectrum, λ_{max} = 261 and 267 nm, agreed with that of these authors.

Samples of NO (commercial purity 99.0%, Matheson) were drawn into all-glass syringes which were pre-flushed with N_2 gas to prevent immediate conversion to NO_2 prior to injection into the chamber. NO_2 was prepared by transferring the measured amount of NO into a glass syringe containing O_2.

Ozone was produced in a Welsbach laboratory ozonizer and collected into two- and five-liter Pyrex bulbs. Depending on the requirements of the experiment, samples with 0.8-1.5% O_3, as analyzed by IR spectroscopy, were obtained by appropriate adjustments of O_2 gas flow and/or voltage applied to the electrodes of this ozonizer.

Experimental Procedure. Each of the compounds under study was introduced into the chamber as a vapor. For liquid samples (trimethylphosphate and 1,3-dichloropropene), the calculated amount of liquid was placed in a two-liter bulb and the vapor was carried into the chamber by a stream of N_2 gas while the sample was being gently warmed. The same procedure was followed for the solid sample (phenyl N-methylcarbamate) with heating to the melting point and a considerably longer period of flushing with purified air. The sample was continuously mixed by fans inside the chamber while being introduced.

The pre-determined amount of O_3 in a calibrated glass bulb or NO/NO_2 in glass syringes was then flushed and stirred into the chamber through the Teflon disperser tube. Uniform mixing of reactants was verified to be complete within two minutes.

The chamber was thoroughly flushed with clean ambient air after each run, and was additionally purged and filled with a total of five volumes of dry (< 10% RH, 293 K) purified air (Doyle et al. 1977) prior to each experiment.

NO and NO_2 were monitored by a Bendix chemiluminescence instrument. For some runs, ozone readings were also obtained using a Dasibi UV absorption ozone monitor to supplement those obtained by infrared measurements.

The growth and decay of all other species were monitored by FT-IR spectroscopy at pathlengths of 200-540 meters and a spectral resolution of 1 cm^{-1}. At these pathlengths, the strong absorptions of H_2O and CO_2 limit the usable infrared spectral windows to the approximate regions

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730–1300, 2000–2300 and 2400–3000 cm^{-1}. Approximately 80 seconds were required to collect the 64 interferograms co-added for each spectrum.

Reactant and product analyses were obtained from the intensities of infrared absorption bands by spectral desynthesis (i.e., successive subtraction of overlapping absorptions by known species). Low noise reference spectra for the reactants and identifiable products were generated for this purpose so as to minimize the increase in the noise level of the residual spectrum with each stage of subtraction.

Infrared Spectra. The vapor phase infrared spectra of trimethylphosphate, phenyl N-methylcarbamate and trans-1,3-dichloropropene in the 720–1360 cm^{-1} spectral region are shown in Figure 32. The absorption bands used for the measurements and their respective absorption coefficients, σ (cm^{-1} atm^{-1}, base e), are as follows:

Phenyl N-methylcarbamate – 1214.0 cm^{-1} ($\sigma = 76$)

Trimethylphosphate – 856.7 cm^{-1} ($\sigma = 29$)

trans-1,3-Dichloropropane – 1241.9 cm^{-1} ($\sigma = 2.7$);

932.9 cm^{-1} ($\sigma = 6.7$)

Results and Discussion

1-Naphyl-N-methylcarbamate

A study of 1-napthyl N-methylcarbamate (commonly known as carbaryl) was attempted. The experiments were conducted in a rectangular Teflon chamber (~8000 liters) which previously housed the long-path optics. Although the vapor pressure of carbaryl has been reported to be ~3 x 10^{-3} mm Hg at 299 K (a saturation concentration of ~6.5 ppm, as noted in Table 22), the solid compound could not be introduced in significant amounts as a vapor into the chamber. Quantities of the finely powered solid were subsequently spread over the Teflon bottom of the chamber. Dark reaction with O$_3$ and irradiation with NO$_x$ were carried out for up to four hours with periodic stirring by fans. No detectable product formation was observed in either case.

In view of the problems associated with introduction of this compound into the vapor phase, further studies were carried out with the homologous compound, phenyl N-methylcarbamate in the ~32,000-liter chamber, as discussed below.

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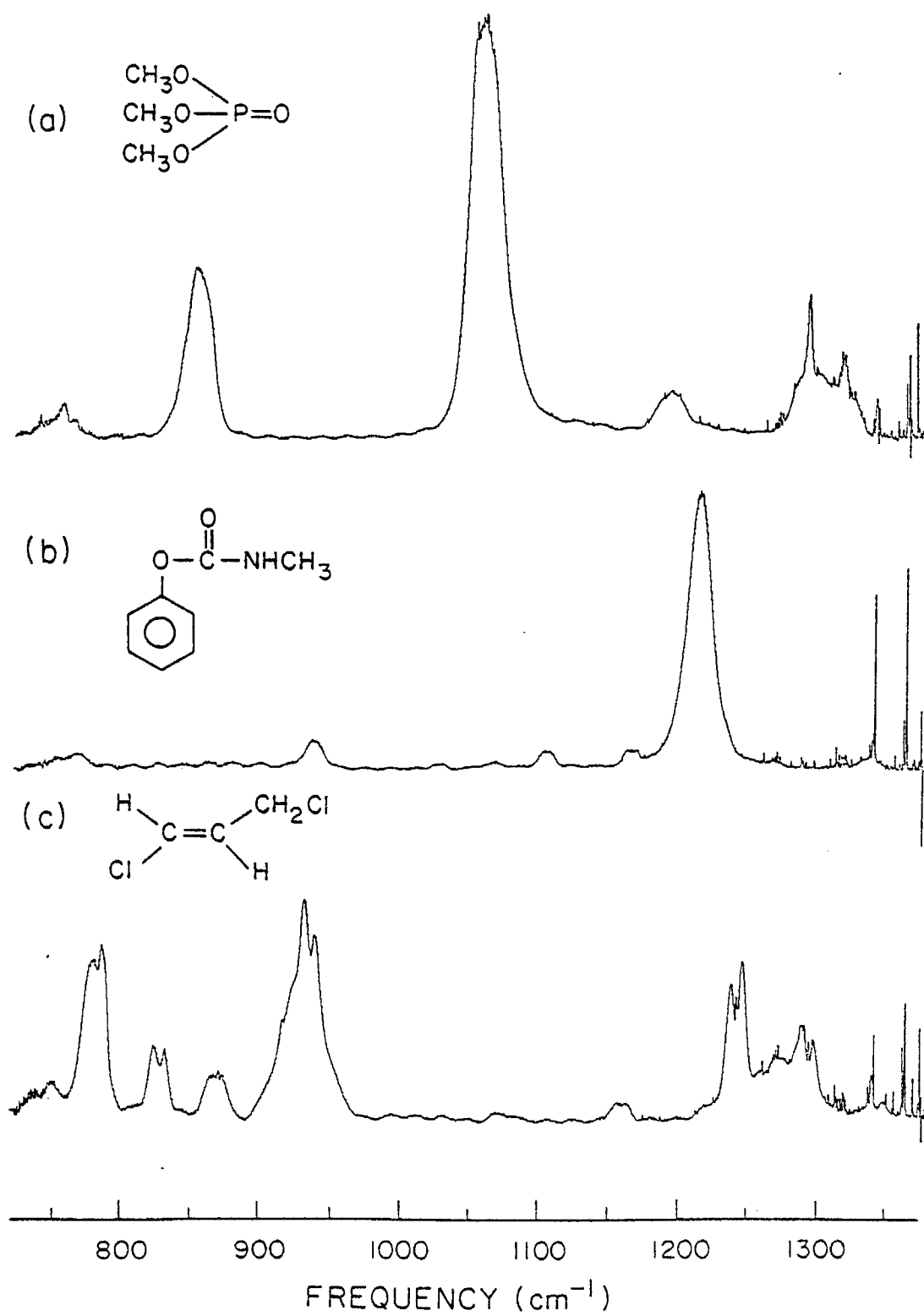
Figure 32. Vapor phase infrared spectra of a) trimethylphosphate,
b) phenyl N-methylcarbamate and c) trans-1,3-dichloro-
propene.

Phenyl N-methylcarbamate

a. O_3 Reaction. Ozone (3.0 ppm) was added to 1.0 ppm of the carbamate in dry air. While no measurable change in O_3 concentration was detected during a 4.5-hour period in the dark, a significant loss of phenyl N-methylcarbamate, corresponding to a rate of $(5.9 \pm 0.4) \times 10^{-4}$ min^{-1}, was observed during this experiment. There were no products detectable in the infrared spectrum. The decay in the carbamate concentration was presumably due to condensation on the walls of the outdoor chamber since the ambient temperature dropped from 297 to 288 K during the course of the experiment (c.f. other experiments below). The vapor phase reaction of phenyl N-methylcarbamate with O_3 is thus either negligible or too slow to be followed by the experimental method employed here.

b. NO_x-Air Photooxidation. The photooxidation of phenyl N-methylcarbamate was studied with initial concentrations of 1.0 ppm carbamate and 0.3 ppm NO_x (0.15 ppm NO_2 and 0.15 ppm NO). Conversion of NO to NO_2 proceeded slowly, with NO consumption complete after 200 minutes, but no O_3 ($\leq$ 0.06 ppm) was observed in the infrared spectra during an additional 60 minutes of irradiation. No measurable change in the carbamate concentration occurred during the first three hours of irradiation when the chamber temperature remained essentially constant at 309 $\pm$ 1 K. However, during the next hour, when the temperature rapidly dropped to 293 K during the afternoon sunlight irradiation, a sharp decrease in the carbamate concentration, amounting to a 33% loss, occurred. This loss is almost certainly due to condensation of the carbamate. The above results indicate that either phenyl N-methylcarbamate is not reactive in irradiated NO_x-air systems, or that when it reacts it acts as a net radical sink, suppressing the OH radical levels generated in this system to a point such that the rate of their reaction with carbamate is too slow to be measured by this long-path FT-IR method over a period of a few hours.

c. OH Radical Rate Constant Determination. For the purposes of measuring the rate constant for the reaction of the OH radical with the carbamate, the reactivity of these relatively inert NO_x-photooxidation systems systems can be greatly enhanced by addition of a reactive component such as m-xylene. This technique has been successfully applied to similar systems in this laboratory to measure rates of reaction with the OH radical.

Essentially, the decays of m-xylene and the compound of interest are measured and since

$$OH + \text{m-xylene} \rightarrow \text{products} \qquad (1)$$

$$OH + \text{reactant} \rightarrow \text{products} \qquad (2)$$

then

$$\ln([\text{m-xylene}]_{t_0}/[\text{m-xylene}]_t) = k_1 \int_{t_0}^{t} [OH]_t \, dt \qquad (I)$$

and

$$\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t) = k_2 \int_{t_0}^{t} [OH]_t \, dt \qquad (II)$$

Hence,

$$\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t) = k_2/k_1 \ln([\text{m-xylene}]_{t_0}/[\text{m-xylene}]_t) \qquad (III)$$

where $[\text{reactant}]_{t_0}$, $[\text{reactant}]_t$ are the reactant concentrations at times t_0 and t, $[\text{m-xylene}]_{t_0}$, $[\text{m-xylene}]_t$ are the corresponding m-xylene concentrations, and k_1 and k_2 are the rate constants for reactions (1) and (2), respectively. Hence, a plot of $\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ against $\ln([\text{m-xylene}]_{t_0}/[\text{m-xylene}]_t)$ should be a straight line of slope k_2/k_1 (Atkinson et al. 1978). Since k_1 is known to be 2.1×10^{-11} cm^3 molecule^{-1} sec^{-1} at 300 K (Atkinson et al. 1979), k_2 may be calculated. This approach assumes that the sole reactions of m-xylene and the reactant are with the OH radical (which is the case for m-xylene). In case of appreciable reaction of the compound of interest with O_3, the experiment must be carried out at high initial NO levels to delay the formation of O_3 and provide sufficient time to permit the measurement of an adequate number of concentration points.

An irradiation experiment was thus conducted in which the initial concentrations of reactants were approximately 0.9 ppm phenyl N-methylcarbamate, 1.4 ppm m-xylene and 0.3 ppm NO_x (0.13 ppm NO + 0.18 NO_2). The reaction was allowed to proceed past the O_3 maximum, after which an additional 0.6 ppm of NO was introduced into the chamber.

Figure 33 shows the observed time-concentration profiles of the carbamate, m-xylene, NO and O_3 during this irradiation. Other products observed were peroxyacetyl nitrate (PAN), HCHO, HCOOH and HNO_3, which are
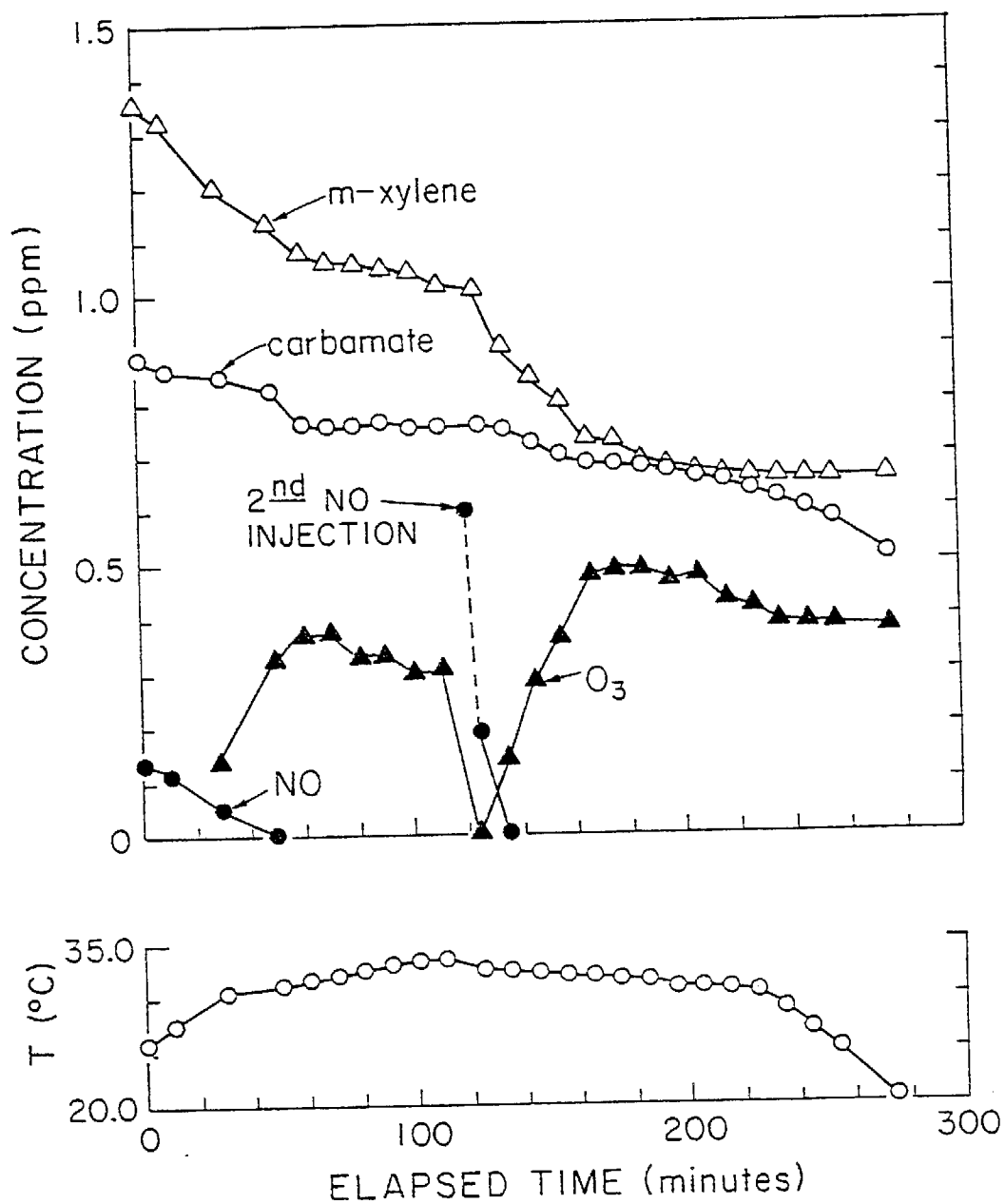
Figure 33. Time-concentration profiles during a NO_x-carbamate-m-xylene-air irradiation.

known products of the NO_x photooxidation of m-xylene. Although ~25% of the carbamate disappeared up to the time when a significant drop in temperature occurred, no products unique to the reaction of phenyl N-methylcarbamate itself could be clearly identified, possibly due to low yields and/or low absorption coefficients of the products formed.

The first 90 minutes following the second NO injection showed a consumption of about 14% carbamate and 35% m-xylene. A near-constant temperature (304.8 $\pm$ 1 K) prevailed during this segment of the experiment, and carbamate losses due to condensation were presumably negligible. The plot of the $\ln(C_o/C_t)$ data for phenyl N-methylcarbamate against those of m-xylene for this period (Figure 34) yields a slope = (k_{xylene})/ $(k_{carbamate})$ of 2.6 $\pm$ 0.3. This corresponds to a rate constant of 8 x 10^{-12} cm^3 molecule^{-1} sec^{-1} at 305 K for the reaction of OH with phenyl N-methylcarbamate.

Trimethylphosphate

a. <u>Reaction with O_3</u>. A mixture of 0.3 ppm trimethylphosphate and 3.0 ppm O_3 did not yield any detectable products or show a significant change in the O_3 concentration during a four-hour dark experiment. Approximately 9% of trimethylphosphate disappeared, corresponding to a loss rate of 3.9 x 10^{-4} min^{-1}, presumably to the chamber walls. The average temperature during the experiment was 298 $\pm$ 3 K.

Subsequently, the decay of 1.4 ppm trimethylphosphate in the chamber was followed for three hours at 295 $\pm$ 3 K under sunlight irradiation. The rate of loss was found to be (4.9 $\pm$ 0.4) x 10^{-4} min^{-1}. Since trimethylphosphate only absorbs very weakly in the actinic region (Benschap and Halmann 1974), and since the measured rate of loss agreed with that found in the dark reaction exposure to O_3, the decay is most probably due to adsorption on the chamber walls.

b. <u>NO_x-Air Photooxidation: Determination of OH Rate Constant</u>. As in the case of phenyl N-methylcarbamate, the reaction in the irradiated mixture of trimethylphosphate alone in the presence of NO_x was too slow to be measured by the present techniques. The rate constant for reaction of trimethylphosphate with OH radicals was determined by carrying out NO_x-air-trimethylphosphate irradiations with added m-xylene. The initial
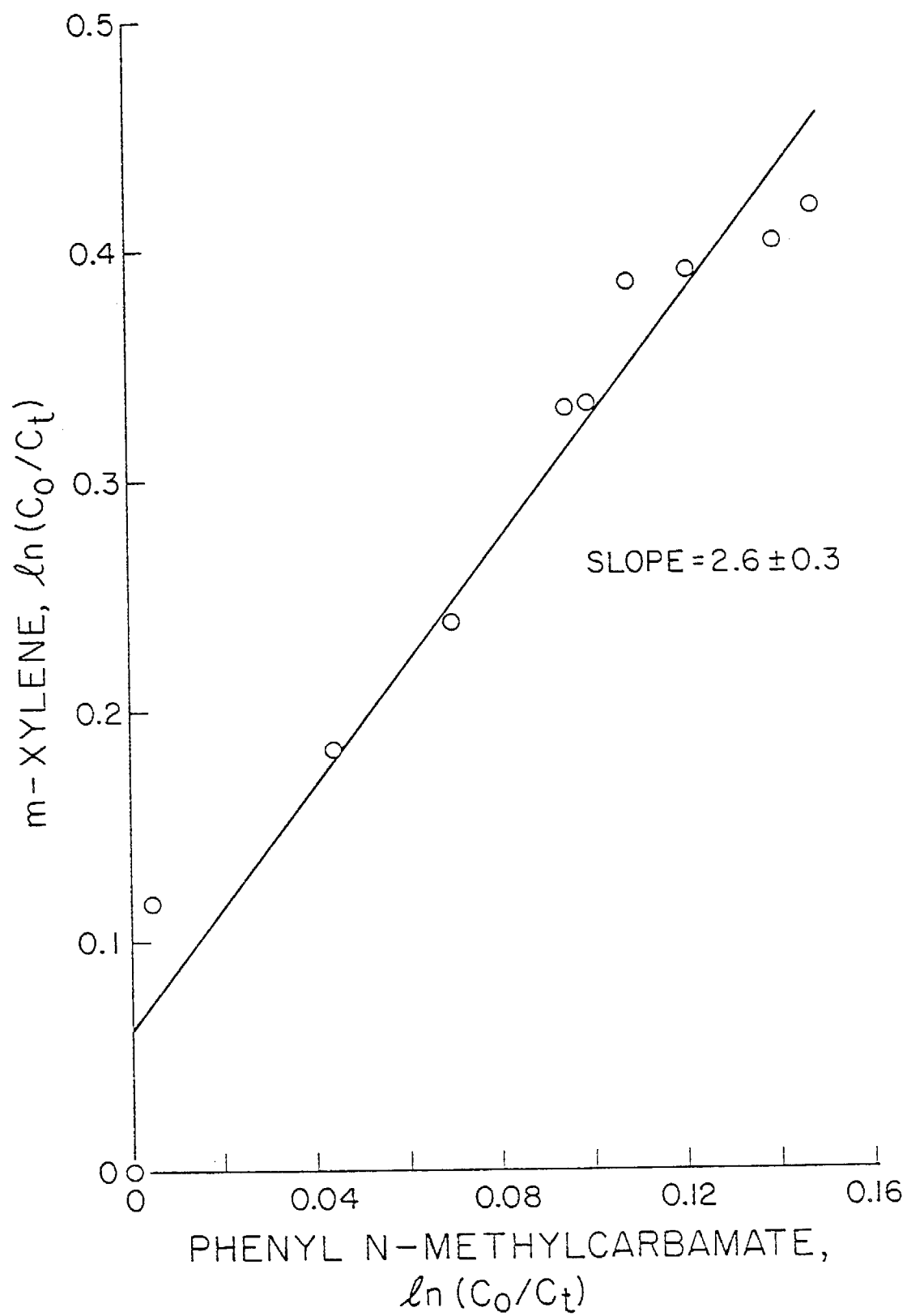
Figure 34. Plots of ln(C$_0$/C$_t$) for m-xylene and phenyl N-methylcarbamate
from a NO$_x$-m-xylene-carbamate-air irradiation.

concentrations employed were: 1.8 ppm trimethylphospate, 1.1 ppm m-xylene and 0.24 ppm NO_x (0.12 ppm each of NO and NO_2).

Figure 35 shows the date plotted in accordance with equation III. The concentrations of trimethylphosphate were corrected for losses according to the measured decay rate of the compound alone (4.9 x 10^{-4} min^{-1} at ~298 K). The value of $(k_{xylene})/(k_{phosphate})$ determined from the plot of Figure 35 is 4.8 $\pm$ 0.4, leading to a rate constant of 4.4 x 10^{-12} cm^3 molecule^{-1} sec^{-1} for the reaction of OH with trimethylphosphate (the error given for the slope does not reflect the additional uncertainty caused by the error in the decay rate constant.) It should be noted that the NO_x photooxidation experiment with added m-xylene was carried out at a significantly higher prevailing temperature (312 $\pm$ 3 K) than that for the decay experiment, and thus the corrections for trimethylphosphate decay which were made in the above analysis may have been over-estimates.

The $(k_{xylene})/$ $(k_{phosphate})$ ratio corresponding to no corrections for wall losses is 2.9 $\pm$ 0.2, leading to k(OH + trimethylphosphate) $\simeq$7 x 10^{-12} cm^3 molecule^{-1} sec^{-1}. Hence, taking an average of the two values obtained leads to an OH radical rate constant of (6 $\pm$ 2) x 10^{-12} cm^3 molecule^{-1} sec^{-1} at 312 $\pm$ 3 K, which is in excellent agreement with that calculated (5.4 x 10^{-12} cm^3 molecule^{-1} sec^{-1} at 305 K) from the formula given by Atkinson et al. (1979) for the reaction of hydroxyl radicals with ethers containing primary C-H bonds.

trans-1,3-Dichloropropene

a. **Reaction with O_3**. The reaction of 5.0 ppm trans-1,3-dichloro-propene and 1.0 ppm O_3 was monitored for three hours in the dark at a nearly constant temperature of 293 K. (It was previously verified that the dichloropropene by itself had no measurable decay in the reaction chamber for comparable periods of time.) A plot of O_3 consumption with time (Figure 36) yielded a slope of (5.0 $\pm$ 0.13) x 10^{-3} min^{-1}. During the same time period, the corresponding loss in dichloropropene amounted to 12.7% of the initial concentration. From the O_3 decay rate data, a rate constant of (1.1 $\pm$ 0.15) x 10^{-3} ppm^{-1} min^{-1} or (7.3 $\pm$ 1.0) x 10^{-19} cm^3 molecule^{-1} sec^{-1} at 293 K can be determined for the reaction of O_3 with trans-1,3-dichloropropene.
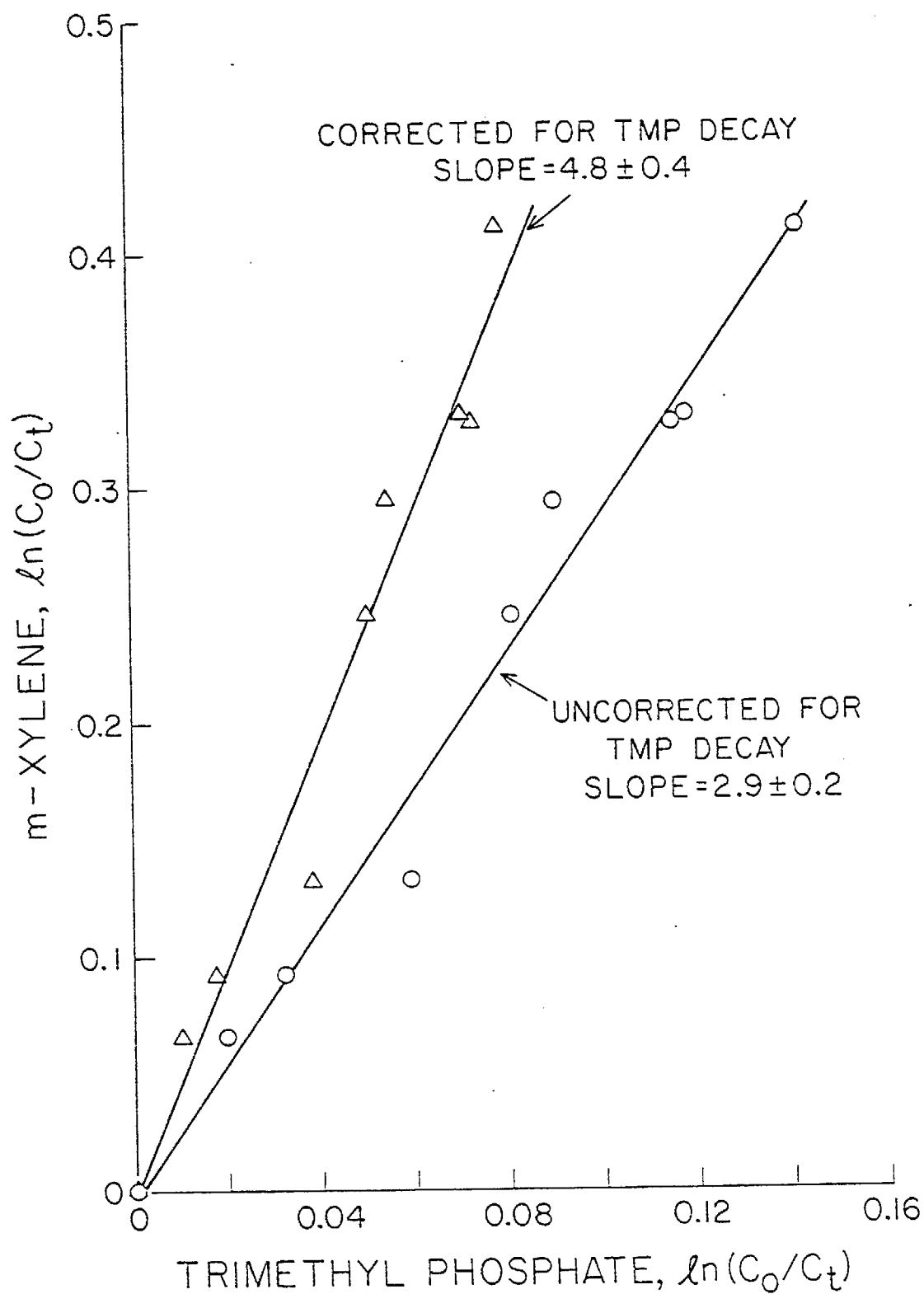
Figure 35. Plots of ln(C₀/Cₜ) for m-xylene and trimethylphosphate (TMP) for a NO$_x$-m-xylene-trimethylphosphate-air irradiation. (See text for explanation of corrected data.)

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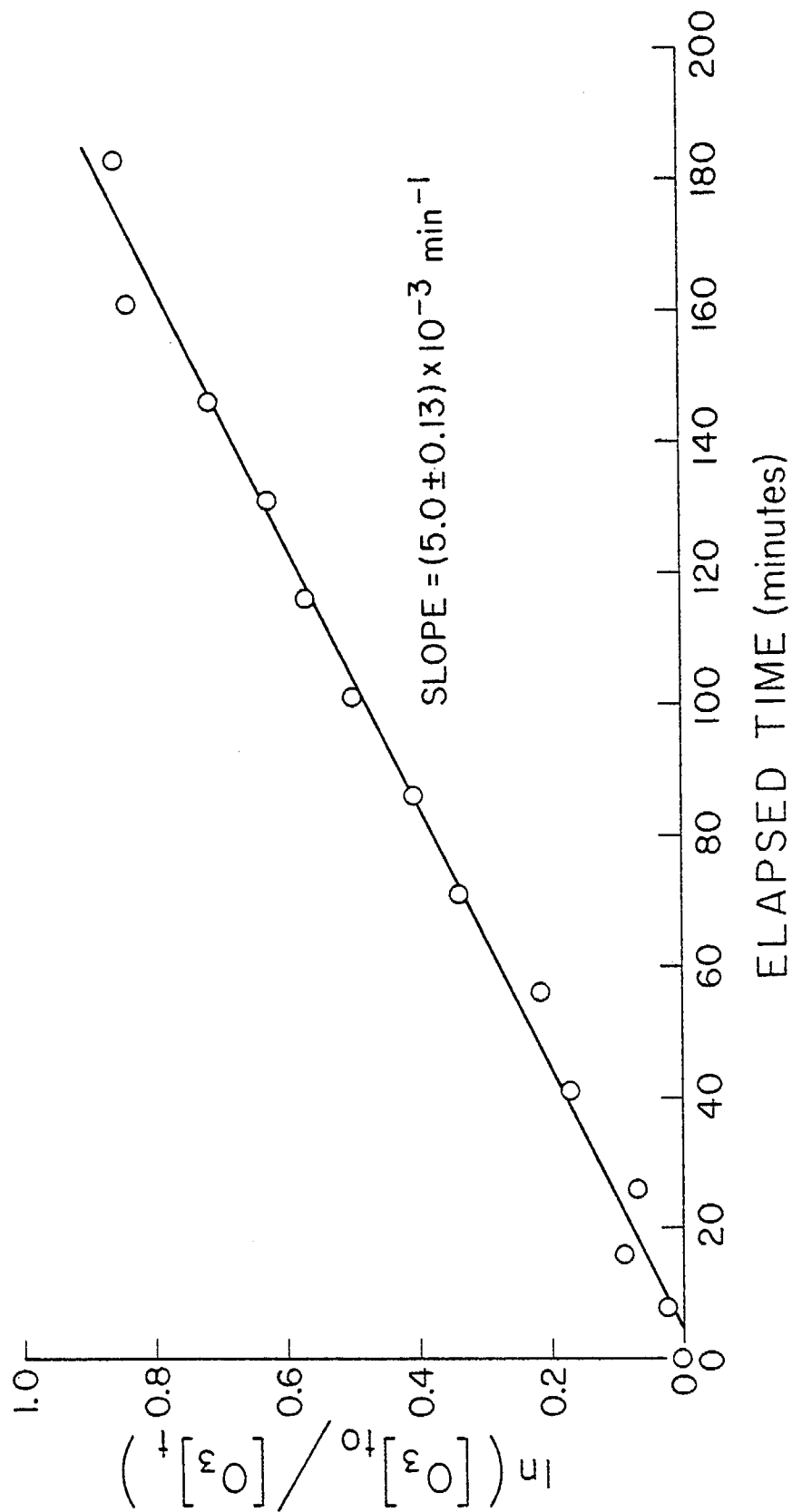
Figure 36. Plot of $\ln([O_3]_{t_o}/[O_3]_t)$ against time for the reaction of O_3 with trans-1,3-dichloropropene.

SLOPE $= (5.0 \pm 0.13) \times 10^{-3}$ min^{-1}

In the second experiment, 2.2 ppm dichloropropene and 2.7 ppm O_3 were reacted. After 90 minutes, a second injection of O_3 (5.0 ppm total O_3 with 1.5 ppm dichloropropene remaining at this point) was made and the rate of consumption of the dichloropropene was monitored for an additional 110 minutes. The rate constant derived for the reaction under excess O_3 was in excellent agreement with that obtained from the first experiment which was carried out in excess dichloropropene. This O_3 rate constant is totally consistent with those for the alkenes (Niki 1979) when the deactivating effect of the substituent Cl atoms is taken into account.

The dichloropropene/ozone stoichiometry was determined to be in the range (1.1–1.5):1 for all conditions of excess O_3, excess dichloropropene, or nearly equimolar initial reactant concentrations, with the higher ratio being reflected earlier in the reaction.

Formylchloride (HCCl) was the major product observed by infrared spectroscopy, but it could not be quantified due to the difficulty in measuring its absorption coefficients. HCl and CO were also observed to be formed, most likely from the facile decomposition of formylchloride.

Product formation can be postulated as proceeding via addition of O_3 to the double bond:

$$\begin{array}{cc}
\overset{\displaystyle O\cdot}{[ClCH_2\overset{|}{C}\text{-}O]\cdot} & \overset{\displaystyle O}{ClCH_2\overset{\|}{C}OH} \\
\uparrow & \\
[ClCH_2\overset{\cdot}{C}HO\overset{\cdot}{O}] & +\ \overset{O}{H\overset{\|}{C}Cl} \\
\uparrow\ a & \\
\end{array}$$

$$ClCH_2CH=CHCl + O_3 \longrightarrow \underset{\underset{H}{|}}{ClCH_2\overset{\overset{O}{\overset{/\ \ \backslash}{\overset{O\quad O}{|\quad\ |}}}}{C}} \underset{\underset{H}{|}}{C\text{-}Cl}$$

$$\downarrow\ b$$

$$\overset{O}{ClCH_2\overset{\|}{C}H}\ +\ [Cl\overset{\cdot}{C}H\overset{\cdot}{O}]$$

$$\downarrow$$

$$[Cl\overset{\overset{O\cdot}{|}}{\underset{\underset{H}{|}}{C}}\text{-}O\cdot]\ \downarrow$$

$$HCl + CO_2$$

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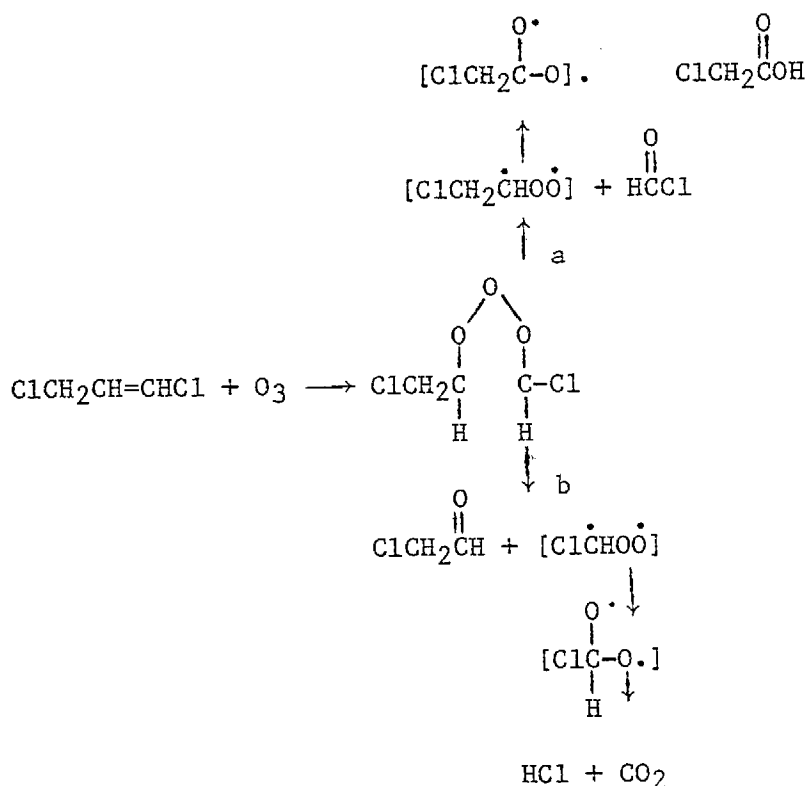
However, within the available infrared spectral windows, no clearly measurable absorption bands could be attributed to either chloroacetaldehyde or chloroacetic acid. If step (a) is the favored pathway, the chloroacetic acid formed could possibly be present only in the vapor phase at very low concentrations, since this compound is a solid at room temperature (m.p. 62.4°C).

b. NO_x-Air Photooxidations: Products and OH Radical Rate Constant. Sunlight irradiated mixtures of trans-1,3-dichloropropene and NO_x in air yielded the same products as those observed for the reaction of O_3 with the dichloropropene both prior to and after O_3 formation. Details of possible reaction mechanisms are expected to be analogous to those proposed in a similar study of chlorinated ethenes (Gay et al. 1976).

Figure 37 shows selected time-concentration data for the irradiation of a mixture with initial concentrations of 2.3 ppm trans-1,3-dichloropropene, 1.9 ppm m-xylene and 2.0 ppm NO_x (1.7 ppm NO and 0.3 ppm NO_2). Not shown are the time-concentration profiles for the known products of m-xylene/NO_x photooxidations, such as PAN, HCHO, HCOOH, and HNO_3. Only the absorbance values (base e) of the 739 cm^{-1} Q-branch at a pathlength of 220 meters are plotted for formylchloride due to lack of absorption coefficients for this compound. A high initial concentration of NO was purposely employed to delay O_3 formation.

It is seen from Figure 37 that NO was rapidly depleted and was followed by a rapid rise in O_3 concentration for t > 50 minutes. For t $\leq$ 50 minutes, O_3 levels were suppressed by excess NO, and hence reaction of O_3 with the dichloropropene was negligible. Hence measurements made during this time period provided valid data points for the parallel reactions of OH with the dichloropropene and m-xylene. After 50 minutes of irradiation, 9.5% and 15.8% of the initial concentrations of trans-1,3-dichloropropene and m-xylene, respectively, were consumed. A plot of equation III for t $\leq$ 50 minutes for dichloropropene and m-xylene yielded $(k_{xylene}/k_{dichloropropene})$ = 1.5 $\pm$ 0.2 This corresponds to a rate constant of 1.4 x 10^{-11} cm^3 molecule^{-1} sec^{-1} for the reaction of OH with trans-1,3-dichloropropene, which is again consistent with the trends for the homologous compounds ethene, vinyl chloride and propene (Atkinson et al. 1979).

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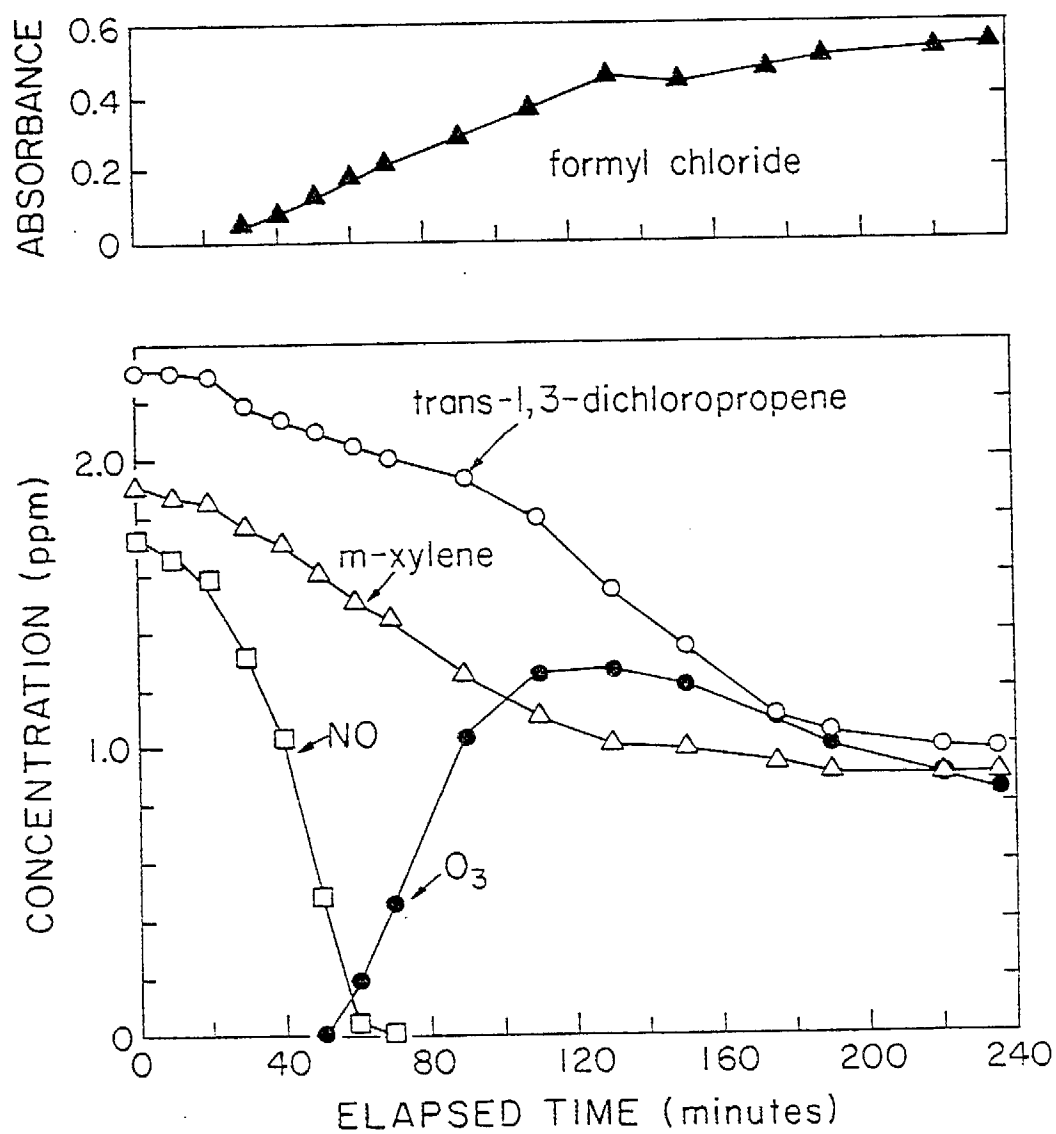
Figure 37. Time-concentration profiles for a NO_x-trans-1,3-
dichloropropene-m-xylene-air irradiation.

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APPENDIX A

Detailed Data Sheets for NO_x-Air Irradiations Concerning

the Chamber- Dependent Radical Source

Index for Appendix A

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Index for Appendix A (continued)

EC-434
NOX-AIR, STANDARD
1980, SEPT 11

CHAMBER PUMPING ABORTED AT 0630
0800: EC PRESSURE =0.2 TORR
0857: DIFF PUMP POWER ON
1118: EC PRESSURE=1.8E-5 TORR
1217: NO, NO2 INJECTED USING VACUUM TECHNIQUE
1248: BEGIN ~40% RH PURE AIR FILL
1315: PROPANE, PROPENE INJECTED

T=0 AT 1430 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.180	0.030	PPT
TS	DORIC-1	29.6	0.3	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.395	PPM
NO2-UNC	T 14B-3	0.075	PPM
PROPANE	DMS-1	0.0110	PPM
PROPENE	DMS-1	0.0115	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	PROFALD PPM 10'C-600	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1345	-45	-----	-----	0.0190	0.0132	0.363	------	-----	------	-----	-----	-----
1 1410	-20	-----	-----	0.0185	0.0131	0.349	------	-----	------	-----	-----	-----
1 1430	0	-----	0.075	0.0110	0.0115	-----	------	29.8	0.0012	1.47	0.000	0.0012
1 1445	15	0.387	0.083	0.0180	0.0117	0.439	0.179	29.8	------	-----	-----	-----
1 1500	30	0.383	0.092	0.0181	0.0107	0.526	0.170	29.2	------	-----	-----	-----
1 1515	45	0.379	0.091	0.0170	0.0093	0.609	0.181	29.2	------	-----	-----	-----
1 1530	60	0.371	0.099	0.0170	0.0084	0.697	0.244	29.3	------	-----	-----	-----
1 1545	75	0.364	0.104	0.0170	0.0075	0.816	0.158	29.8	------	-----	-----	-----
1 1600	90	0.354	0.106	0.0170	0.0070	0.893	0.177	29.5	------	-----	-----	-----
1 1615	105	0.346	0.113	0.0170	0.0064	0.979	0.154	29.9	0.0023	1.69	-----	-----
1 1630	120	0.336	0.118	0.0162	0.0056	1.054	------	29.9	------	-----	0.040	0.0071

------ NO DATA TAKEN

141

EC-435
NOX-AIR, STANDARD
1980,SEPT 16

1319: NO, NO2 INJECTED USING VACUUM TECHNIQUE
1355: BEGIN ~40% RH PURE AIR FILL
1455: PROPANE, PROPENE INJECTED

T=0 AT 1530 FDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.189	0.030	PPT
TS	DORIC-1	30.9	0.6	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.382	PPM
NO2-UNC	T 14B-3	0.087	PPM
PROPANE	DMS-1	0.0190	PPM
PROPENE	DMS-1	0.0124	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1520	-10	------	------	0.0196	0.0134	0.3800	------	30.3	------	------	------
1 1530	0	0.382	0.087	------	------	------	------	29.9	0.95	0.013	0.0010
1 1545	15	0.380	0.092	0.0183	0.0113	0.4820	0.179	31.8	------	------	------
1 1600	30	0.373	0.093	0.0178	------ R	------	------	30.6	------	------	------
1 1615	45	0.368	0.095	0.0188	0.0098	0.6560	0.160	30.9	------	------	------
1 1630	60	0.361	0.099	0.0173	0.0083	0.7340	0.214	31.2	------	------	------
1 1645	75	0.356	0.099	0.0178	0.0078	0.8380	0.150	31.4	------	------	------
1 1700	90	0.354	0.101	0.0181	0.0073	0.9110	0.224	30.6	------	------	------
1 1715	105	0.347	0.105	0.0180	0.0065	1.020	0.205	31.1	------	------	------
1 1730	120	0.339	0.105	0.0184	0.0060	1.120	------	31.2	0.93	0.021	0.0051

------ NO DATA TAKEN

NOTES

R   POINT REJECTED

142

EC-436
NOX-AIR, HIGH NOX
1980, SEPT 17

CHAMBER PUMPING ABORTED AUTOMATICALLY AT 0250
0820: EC PRESSURE=0.5 TORR
DIFF PUMP ON

0914: EC PRESSURE=7.2E-5 TORR
0952: NO, NO2 INJECTION USING VACUUM TECHNIQUE
1006: BEGIN ~45% RH PURE AIR FILL
1020: PROPANE, PROPENE INJECTED

T=0 AT 1045 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.108	0.016	PPT
TS	DORIC-1	29.8	1.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	1.426	PPM
NO2-UNC	T 14B-3	0.364	PPM
PROPANE	DMS-1	0.0123	PPM
PROPENE	DMS-1	0.0077	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 1024	-21	-----	-----	-----	-----	-----	-----	-----	2.24	0.0062	0.0117	0.0100
1 1045	0	1.426	0.364	0.0123	0.0077	0.4700	-----	27.4	-----	-----	-----	-----
1 1100	15	1.393	0.336	0.0132	0.0078	0.5276	0.089	29.3	-----	-----	-----	-----
1 1115	30	1.377	0.343	0.0133	0.0075	0.5709	0.101	29.6	-----	-----	-----	-----
1 1130	45	1.361	0.328	0.0129	0.0069	0.6199	0.138	29.9	-----	-----	-----	-----
1 1145	60	1.353	0.320	0.0128	0.0064	0.6872	0.113	30.0	-----	-----	-----	-----
1 1200	75	1.353	0.308	0.0133	0.0063	0.7423	0.102	30.0	-----	-----	-----	-----
1 1215	90	1.345	0.308	0.0130	0.0059	0.7919	0.116	30.2	-----	-----	-----	-----
1 1230	105	1.345	0.301	0.0128	0.0055	0.8486	0.098	30.9	-----	-----	-----	-----
1 1245	120	1.328	0.292	0.0127	0.0052	0.8965	-----	31.1	2.23	0.0058	0.0119	0.0099

------ NO DATA TAKEN

143

EC-436
NOX-AIR, HIGH NOX
1980, SEPT 17

	CLOCK TIME	ELAPSED TIME (MIN)	ACETALD PPM 10'C-600
DY HR.			
1 1024	-21	0.0010	
1 1245	120	0.0035	

------ NO DATA TAKEN

144

EC-437
NOX-AIR, LOW NOX
1980, SEPT 1B

CHAMBER EVACUATED TO 3.2E-5 TORR PREVIOUS NIGHT, BUT NOT PUMPED ON
OVERNIGHT
0730: EC PRESSURE=0.5 TORR
0826: DIFF PUMP ON
1134: EC PRESSURE=2.9E-5 TORR
1136: NO, NO2 INJECTED USING VACUUM TECHNIQUE
1209: BEGIN ~42% RH PURE AIR FILL
      PROPANE, PROPENE INJECTED

T=0 AT 1315 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.201	0.029	PPT
TS	DORIC-1	31.3	0.6	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.164	PPM
NO2-UNC	T 14B-3	0.037	PPM
PROPANE	DMS-1	0.0122	PPM
PROPENE	DMS-1	0.0105	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 1235	-40	----	----	0.0126	0.0108	0.1540	----	----	----	----	----	----
1 1236	-39	----	----	----	----	----	----	----	1.86	0.0029	0.0051	0.0036
1 1255	-20	----	----	0.0126	0.0108	0.1480	----	----	----	----	----	----
1 1315	0	----	----	0.0122	0.0105	0.1530	0.181	----	----	----	----	----
1 1318	3	0.160	0.040	----	----	----	----	32.2	----	----	----	----
1 1330	15	0.159	0.040	0.0124	0.0097	0.2410	0.175	32.0	----	----	----	----
1 1345	30	0.153	0.043	0.0124	0.0089	0.3260	0.172	31.1	----	----	----	----
1 1400	45	0.149	0.042	0.0124	0.0083	0.4100	0.183	30.9	----	----	----	----
1 1415	60	0.144	0.049	0.0126	0.0076	0.4990	0.197	30.5	----	----	----	----
1 1430	75	0.141	0.053	0.0121	0.0067	0.5950	0.216	31.5	----	----	----	----
1 1445	90	0.135	0.059	0.0123	0.0061	0.7000	0.236	30.9	----	----	----	----
1 1500	105	0.130	0.061	0.0121	0.0054	0.8150	0.246	30.9	----	----	----	----
1 1515	120	0.123	0.065	0.0118	0.0046	0.9350	----	31.4	1.86	0.0025	0.0051	0.0037

------ NO DATA TAKEN

EC-437
NOX-AIR, LOW NOX
1980, SEPT 18

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	BENZENE PPM 10'C-600	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600	BUTYRAL PPM 10'C-600
1 1236	-39	0.0002	0.0008	0.0001	0.0005	0.0004
1 1515	120	0.0002	0.0051	0.0004	0.0021	0.0005

------ NO DATA TAKEN

EC-438
NOX-AIR, HIGH NO2/NO
1980, SEPT 19

CHAMBER EVACUATED TO 8.2 E-5 TORR PREVIOUS NIGHT, BUT NOT PUMPED OUT
OVERNIGHT
0800: PRESSURE= 1 TORR
0807: DIFF PUMP ON
1007: EC PRESSURE 7.5E-5 TORR
NO, NO2 INJECTED USING VACUUM TECHNIQUE
1023: BEGIN ~45% RH PURE AIR FILL
1035: PROPANE, PROPENE INJECTED

T=0 AT 1115 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL	DORIC-1	0.163	0.060	PPT
TS		29.3	0.5	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.131	PPM
NO2-UNC	T 14B-3	0.469	PPM
PROPANE	DMS-1	0.0146	PPM
PROPENE	DMS-1	0.0103	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 1052	-23	------	------	0.0144	0.0101	0.3535	------	------	------	0.0055	0.0096	0.0060
1 1103	-12	------	------	0.0143	0.0101	0.3519	------	------	2.08	------	------	------
1 1115	0	0.131	0.469	0.0146	0.0103	0.3464	0.268	28.3	------	------	------	------
1 1130	15	0.184	0.184	0.0144	0.0089	0.4768	0.224	30.0	------	------	------	------
1 1145	30	0.197	0.197	0.0144	0.0080	0.5860	0.109	29.2	------	------	------	------
1 1200	45	0.207	0.207	0.0146	0.0077	0.6390	0.122	29.2	------	------	------	------
1 1215	60	0.218	0.218	0.0142	0.0070	0.6983	0.138	29.2	------	------	------	------
1 1230	75	0.224	------	0.0143	0.0066	0.7657	0.152	29.3	------	------	------	------
1 1245	90	0.231	------	0.0137	0.0059	0.8396	0.126	29.3	------	------	------	------
1 1300	105	0.239	------	0.0139	0.0057	0.9012	------	29.6	2.05	0.0051	0.0100	0.0063

------   NO DATA TAKEN

147

EC-438
NOX-AIR, HIGH NO2/NO
1980, SEPT 19

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	BENZENE PPM 10'C-600	MEK PPM 10'C-600	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600	TOLUENE PPM 10'C-600
1 1052	-23	0.0023	0.0030	0.0001	0.0003	0.0017	0.0002	0.0011	0.0014
1 1103	-12	-------	-------	-------	-------	-------	-------	-------	-------
1 1115	0	-------	-------	-------	-------	-------	-------	-------	-------
1 1130	15	-------	0.0030	-------	-------	-------	-------	-------	-------
1 1145	30	-------	0.0030	-------	-------	-------	-------	-------	-------
1 1200	45	-------	0.0030	-------	-------	-------	-------	-------	-------
1 1215	60	-------	0.0030	-------	-------	-------	-------	-------	-------
1 1230	75	-------	0.0030	-------	-------	-------	-------	-------	-------
1 1245	90	-------	0.0029	-------	-------	-------	-------	-------	-------
1 1300	105	0.0022	0.0030	0.0002	-------	0.0039	0.0003	0.0026	0.0001

------- NO DATA TAKEN

148

EC-439
NOX-AIR, DRY, UNCONDITIONED CHAMBER
1980, SEP 26

SEPT. 25
 0920: BEGIN HEATING CHAMBER
 1010: BEGIN EVACUATING CHAMBER
 1424: T=356K, PRESSURE= 4.8E-5 TORR
 1706: T=355K, PRESSURE= 1.3E-5 TORR
SEPT. 26
 0728: T=355K, PRESSURE=6.3E-6 TORR
       REFRIGERATION ON
 0937: T=304K, PRESSURE= 1.4E-4 TORR
 0937: START LIQUID N2 EVAPORATE FILL TO 20 TORR
 0943: NO, NO2 INJECTED USING VACUUM TECHNIQUE
 0958: START LIQUID N2 EVAPORATE FILL TO ~586 TORR
 1021: COMPLETE FILL WITH LIQUID O2 EVAPORATE
       PROFANE, PROFENE INJECTED

T=0 AT 1130 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL	DORIC-1	0.281	0.080	PPT
TS		30.1	0.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.387	PPM
NO2-UNC	T 14B-3	0.081	PPM
PROFANE	DMS-1	0.0242	PPM
PROFENE	DMS-1	0.0108	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1040	-50	------	------	0.0245	0.0001	------	------	------	------	------	------
1 1109	-21	------	------	0.0250	0.0111	------	------	------	------	------	------
1 1119	-11	------	------	0.0250	0.0111	------	------	------	------	------	0.0250
1 1130	0	0.387	0.081	0.0242	0.0108	0.8041	0.365	29.6	1.18	0.025	------
1 1145	15	0.386	0.079	0.0238	0.0089	0.9817	0.354	30.5	------	------	------
1 1200	30	0.384	0.075	0.0211 A	0.0067	1.154	0.342	29.9	------	------	------
1 1215	45	0.382	0.072	0.0234	0.0062	1.321	0.238	29.5	------	------	------
1 1230	60	0.383	0.069	0.0221	0.0052	1.437	0.289	30.2	------	------	------
1 1245	75	0.380	0.067	0.0231	0.0048	1.578	0.226	30.0	------	------	------
1 1300	90	0.375	0.068	0.0222	------	------	------	30.5	------	------	------
1 1315	105	0.374	0.067	0.0226	0.0037	1.798	0.149	30.5	------	------	------
1 1330	120	0.371	0.070	0.0208	0.0032	1.871	------	30.2	1.20	0.015	0.0146

------ NO DATA TAKEN

149

EC-439
NOX-AIR, DRY, UNCONDITIONED CHAMBER
1980, SEP 26

NOTES

A   ANAMOLOUSLY LOW!

EC-440
NOX-AIR, HIGH NO
1980,OCT 1

0825: NO2 INJECTED USING VACUUM TECHNIQUE
0853: NO INJECTED USING VACUUM TECHNIQUE
0857: BEGIN ~45% RH PURE AIR FILL
      PROPANE, PROPENE INJECTED

T=0 AT 930 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.157	0.091	PPT
TS	DORIC-1	30.5	0.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.674	PPM
NO2-UNC	T 14B-3	0.084	PPM
PROPANE	DMS-1	0.0156	PPM
PROPENE	DMS-1	0.0103	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN10001SD
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 917	-13	------	------	0.0094	0.0061	------	------	------	------	------	------
1 930	0	0.674	0.084	0.0156	0.0103	0.4160	0.027	29.8	1.36	0.036	0.0016
1 945	15	0.667	0.089	0.0148	0.0096	0.4290	0.150	30.5	------	------	------
1 1000	30	0.658	0.091	0.0149	0.0090	0.5020	0.222	30.2	------	------	------
1 1015	45	0.653	0.089	0.0154	0.0083	0.6100	0.142	30.5	------	------	------
1 1030	60	------ R	0.095	0.0138	0.0070	0.6790	0.150	30.2	------	------	------
1 1045	75	0.642	0.095	0.0147	0.0069	0.7520	0.086	30.5	------	------	------
1 1100	90	0.633	0.103	0.0132	0.0060	0.7940	0.335	30.7	------	------	------
1 1115	105	0.625	0.104	0.0144	0.0055	0.9570	0.142	31.0	------	------	------
1 1130	120	0.611	0.109	0.0140	0.0050	1.026	------	31.1	1.39	------	0.0036

------ NO DATA TAKEN

NOTES

R   POINT REJECTED

151

EC-441
NOX-AIR, STANDARD
1980,OCT 2

0825: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0845: BEGIN ~45 RH PURE AIR FILL
1015: PROPANE, PROPENE INJECTED

T=0 AT 1100 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.196	0.051	PPT
TS	DORIC-1	31.0	2.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.431	PPM
NO2-UNC	T 14B-3	0.104	PPM
PROPANE	DMS-1	0.0147	PPM
PROPENE	DMS-1	0.0105	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3*	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1025	-35	------	------	0.0155	0.0110	0.3390	------	------	------	------	------
1 1040	-20	------	------	------	0.0108	------	------	------	------	------	------
1 1050	-10	------	------	0.0152	0.0108	0.3400	------	------	------	------	0.0018
1 1100	0	0.431	0.104	0.0147	0.0105	0.3300	0.312	27.4	3.90	0.015	------
1 1115	15	0.424	0.104	0.0148	0.0091	0.4820	0.175	28.8	------	------	------
1 1130	30	0.417	0.106	0.0149	0.0084	0.5670	0.193	29.9	------	------	------
1 1145	45	0.411	0.109	0.0143	0.0074	0.6610	0.222	30.6	------	------	------
1 1200	60	0.405	0.110	0.0142	0.0066	0.7690	0.150	30.7	------	------	------
1 1215	75	0.401	0.114	0.0141	0.0061	0.8420	0.175	32.2	------	------	------
1 1230	90	0.393	0.114	0.0142	0.0056	0.9270	0.172	32.6	------	------	------
1 1245	105	0.386	0.118	0.0142	0.0051	1.011	0.172	33.2	------	------	------
1 1300	120	0.379	0.124	0.0138	0.0046	1.095	------	33.6	4.00	0.019	0.0047

------- NO DATA TAKEN

EC-442
NOX-AIR HIGH NO2/NO
1980, OCT 3

0819: NO,NO2 INJECTED VACUUM TECHNIQUE
0837: BEGIN ~50% RH PURE AIR FILL
1008: PROPANE, PROPENE INJECTION

T=0 AT 1115 PDT

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL	DORIC-1	0.232	0.128	PPT
TS	DORIC-1	29.8	0.5	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.117	PPM
NO2-UNC	T 14B-3	0.369	PPM
PROPANE	DMS-1	0.0159	PPM
PROPENE	DMS-1	0.0100	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	BENZENE PPM 10'C-600	MEK PPM 10'C-600	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600
1 1041	-34	-----	-----	0.0166	0.0105	------	-------	-----	0.0003	0.0002	0.0028	0.0001
1 1057	-18	-----	-----	0.0161	0.0103	------	-------	-----	------	------	------	------
1 1105	-10	-----	-----	-----	0.0100	0.4610	-------	28.8	------	------	------	------
1 1115	0	0.117	0.369	0.0159	0.0100	------	0.524	29.8	------	------	------	------
1 1116	1	0.356	0.322	-----	-----	------	0.287	29.5	------	------	------	------
1 1130	15	0.153	0.297	0.0152	0.0074	0.7200	0.253	29.8	------	------	------	------
1 1145	30	0.162	0.270	0.0150	0.0063	0.8600	0.177	29.8	------	------	------	------
1 1200	45	0.164	0.258	0.0156	0.0058	0.9830	0.155	30.0	------	------	------	------
1 1215	60	0.168	0.245	0.0152	0.0052	1.069	0.155	30.0	------	------	------	------
1 1230	75	0.172	0.236	0.0153	0.0049	1.149	0.155	30.0	------	------	------	------
1 1245	90	0.173	0.227	0.0153	0.0045	1.211	0.155	30.5	------	------	------	------
1 1300	105	0.175	0.218	0.0153	0.0042	1.289	0.155	30.5	------	------	------	------
1 1315	120	0.173	0.213	0.0155	0.0039	1.376	-------	30.5	0.0002	------	0.0045	------

------ NO DATA TAKEN

EC-442
NOX-AIR HIGH NO2/NO
1980, OCT 3

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETONE PPM 10'C-600
1 1041	-34	0.0011
1 1315	120	0.0020

------ NO DATA TAKEN

EC-443
NOX-AIR DRY
1980,OCT 7

0927: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0947: BEGIN LIQUID N2 EVAPORATE FILL TO ~586 TORR
1019: COMPLETE FILL WITH LIQUID O2 EVAPORATE
1023: PROPANE, PROPENE INJECTED

T=0 AT 1115 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.109	0.035	PPT
TS	DORIC-1	30.1	0.8	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.411	PPM
NO2-UNC	T 14B-3	0.099	PPM
PROPANE	DMS-1	0.0449	PPM
PROPENE	DMS-1	0.0102	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1035	-40	-----	-----	-----	0.0103	-----	-----	-----	-----	-----	-----
1 1049	-26	-----	-----	0.0442	0.0102	1.461	-----	-----	-----	-----	-----
1 1059	-16	-----	-----	0.0433	0.0100	1.466	-----	-----	-----	-----	-----
1 1101	-14	0.411	0.095	-----	-----	-----	-----	29.9	-----	-----	-----
1 1112	-3	0.411	0.096	0.0449	0.0102	1.477	-----	29.1	-----	-----	-----
1 1115	0	0.411	0.099	0.0427	0.0093	1.518	0.084	28.8	-----	-----	-----
1 1130	15	0.409	0.095	0.0433	0.0090	1.573	0.113	29.9	0.94	0.020	0.0022
1 1145	30	0.409	0.099	0.0432	0.0085	1.621	0.099	29.6	-----	-----	-----
1 1200	45	0.407	0.095	0.0372	0.0069	1.681	0.123	30.0	-----	-----	-----
1 1215	60	0.405	0.095	0.0406	0.0071	1.746	0.133	29.8	-----	-----	-----
1 1230	75	0.405	0.092	0.0403	0.0068	1.778	0.066	30.5	-----	-----	-----
1 1245	90	0.405	0.099	0.0424	0.0069	1.818	0.082	30.7	-----	-----	-----
1 1300	105	0.399	0.099	0.0421	0.0063	1.903	0.175	31.1	-----	-----	-----
1 1315	120	0.397	0.096	-----	-----	-----	-----	31.4	1.07	0.008	0.0027

----- NO DATA TAKEN

EC-444
NOX-AIR, DRY
1980,OCT 8

0904: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0925: BEGIN LIQUID N2 EVAPORATE FILL TO ~590 TORR
1000: COMPLETE FILL WITH LIQUID O2 EVAPORATE
1017: PROFANE, PROPENE INJECTED

T=0 AT 1100 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.100	0.012	PPT
TS	DORIC-1	30.7	0.5	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.413	PPM
NO2-UNC	T 14B-3	0.114	PPM
PROFANE	DMS-1	0.0340	PPM
PROPENE	DMS-1	0.0108	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000150
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

DY NR.	CLOCK TIME	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1	1025	-35	-----	-----	-----	0.0108	-----	-----	-----	-----	-----	-----
1	1035	-25	-----	-----	0.0342	0.0108	1.151	-----	-----	-----	-----	-----
1	1046	-14	0.413	0.113	-----	-----	-----	-----	31.1	-----	-----	-----
1	1048	-12	-----	-----	0.0346	0.0109	1.151	-----	-----	-----	-----	-----
1	1051	-9	0.415	0.110	-----	-----	-----	0.103	31.1	-----	-----	-----
1	1100	0	0.413	0.114	0.0340	0.0108	1.146	0.117	30.2	0.86	0.020	0.00184
1	1115	15	0.411	0.109	0.0331	0.0100	1.196	0.092	30.7	-----	-----	-----
1	1130	30	0.407	0.113	0.0338	0.0096	1.253	0.092	29.9	-----	-----	-----
1	1145	45	0.405	0.106	0.0338	0.0092	1.298	0.117	29.9	-----	-----	-----
1	1200	60	0.405	0.109	0.0331	0.0086	1.343	0.082	30.6	-----	-----	-----
1	1215	75	0.401	0.102	0.0340	0.0084	1.400	0.103	30.7	-----	-----	-----
1	1230	90	0.401	0.104	0.0336	0.0079	1.440	0.097	30.9	-----	-----	-----
1	1245	105	0.397	0.106	0.0340	0.0076	1.490	-----	31.0	-----	-----	-----
1	1300	120	0.393	0.110	0.0335	0.0072	1.537	-----	31.1	0.92	0.013	0.00307

----- NO DATA TAKEN

EC-445
NOX-AIR, H2O SATURATED
1980,OCT 9

0955: NO, NO2 INJECTED USING VACUUM TECHNIQUE
1017: BEGIN WET PURE AIR FILL (WET BULB T=304K, DRY BULB=310K;
      SATURATES AT 303K)
1105: PROPANE, PROPENE INJECTED

T=0 AT 1245 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.616	0.138	PPT
TS	DORIC-1	31.4	0.5	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.411	PPM
NO2-UNC	T 14B-3	0.049	PPM
PROPANE	DMS-1	0.0132	PPM
PROPENE	DMS-1	0.0106	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1220	-25	-----	-----	0.0131	0.0106	0.2060	-----	-----	-----	-----	-----
1 1223	-22	0.405	0.049	-----	-----	-----	-----	32.1	-----	-----	-----
1 1232	-13	-----	-----	0.0131	0.0106	0.2060	-----	-----	-----	-----	-----
1 1235	-10	0.409	0.049	-----	-----	-----	-----	32.2	-----	-----	-----
1 1245	0	0.411	0.049	0.0132	0.0106	0.2120	0.846	30.7	4.26	0.017	0.00524
1 1300	15	0.365	0.092	0.0127	0.0068	0.6240	0.770	30.9	-----	-----	-----
1 1315	30	0.332	0.120	0.0124	0.0045	0.9990	0.641	30.9	-----	-----	-----
1 1330	45	0.312	0.136	0.0121	0.0033	1.311	0.610	31.0	-----	-----	-----
1 1345	60	0.298	0.142	0.0119	0.0024	1.608	0.585	31.1	-----	-----	-----
1 1400	75	0.287	0.150	0.0119	0.0018	1.893	0.466	31.4	-----	-----	-----
1 1415	90	0.276	0.151	0.0114	0.0014	2.120	0.567	31.5	-----	-----	-----
1 1430	105	0.266	0.154	0.0115	0.0010	2.396	0.441	31.8	-----	0.042	-----
1 1445	120	0.258	0.154	0.0112	0.0008	2.611	-----	32.0	-----	-----	0.00803

----- = NO DATA TAKEN

157

EC-446
NOX-AIR, HIGH RH
1980,OCT 10

0754: NO ,NO2 INJECTED USING VACUUM TECHNIQUE
0812: BEGIN ~80% RH PURE AIR FILL
0910: PROPANE, PROPENE INJECTED

T=0 AT 1030 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.488	0.083	PPT
TS	DORIC-1	30.4	1.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.387	PPM
NO2-UNC	T 14B-3	0.059	PPM
PROPANE	DMS-1	0.0128	PPM
PROPENE	DMS-1	0.0088	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1000	-30	0.393	0.059	0.0128	0.0089	0.3610	------	32.0	------	------	------
1 1015	-15	0.393	0.057	0.0131	------	------	------	31.7	------	------	------
1 1030	0	0.387	0.057	0.0128	0.0088	0.3770	0.667	29.8	2.71	0.014	0.00235
1 1045	15	0.373	0.073	0.0130	0.0064	0.7020	0.452	30.3	------	------	------
1 1100	30	0.357	0.079	0.0126	0.0050	0.9220	0.534	28.1	------	------	------
1 1115	45	0.352	0.088	0.0126	0.0038	1.182	0.437	29.5	------	------	------
1 1130	60	0.350	0.095	0.0124	0.0031	1.395	0.474	30.2	------	------	------
1 1145	75	0.339	0.102	0.0121	0.0024	1.626	0.460	30.6	------	------	------
1 1200	90	0.328	0.099	0.0123	0.0019	1.850	0.394	30.6	------	------	------
1 1215	105	0.322	0.104	0.0115	0.0015	2.042	0.487	30.9	------	------	------
1 1230	120	0.312	0.109	0.0114	0.0012	2.279	------	30.9	------	0.021	0.00425

------ NO DATA TAKEN

158

EC-447
NOX-AIR, T=324K, STANDARD
1980,OCT 13

0905: NO, NO2 INJECTED USING VACUUM TECHNIQUE
1004: BEGIN WET PURE AIR FILL (WET BULB TEMP=310K, ~50% RH AT 324K)
1045: PROPANE, PROPENE INJECTED

T=0 AT 1130 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.487	0.143	PPT
TS	DORIC-1	50.2	0.9	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.442	PPM
NO2-UNC	T 14B-3	0.071	PPM
PROPANE	DMS-1	0.0135	PPM
PROPENE	DMS-1	0.0118	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1107	-23	----	----	0.0136	0.0118	0.1360	----	----	----	----	----
1 1120	-10	----	----	0.0135	0.0117	0.1370	----	----	----	----	----
1 1130	0	0.442	0.071	0.0135	0.0118	0.1340	0.593	48.4	0.56	0.008	0.00275
1 1145	15	0.423	0.091	0.0133	0.0087	0.4230	0.585	49.4	----	----	----
1 1200	30	0.405	0.106	0.0130	0.0064	0.7080	0.565	49.7	----	----	----
1 1215	45	0.389	0.124	0.0128	0.0048	0.9830	0.281	50.0	----	----	----
1 1230	60	0.368	0.142	0.0126	0.0037	1.120	0.686	50.1	----	----	----
1 1245	75	0.350	0.151	0.0121	0.0028	1.454	0.474	50.7	----	----	----
1 1300	90	0.334	0.164	0.0124	0.0023	1.685	0.376	51.1	----	----	----
1 1315	105	0.314	0.173	0.0119	0.0018	1.868	0.339	51.1	----	----	----
1 1330	120	0.298	0.181	0.0117	0.0015	2.033	----	51.4	0.68	0.018	0.00946

------ NO DATA TAKEN

159

EC-448
NOX-AIR, T=324K, STANDARD
1980 OCT. 14

0837: PUMPING ABORTED DURING NIGHT. EC PRESSURE=200 MICRONS
0915: DIFF. PUMP ON LINE
0920: PRESSURE= 6E-5 TORR.
0924: NO, NO2 INJECTED USING VACUUM TECHNIQUE,
0940: BEGIN WET (T=300K) PURE AIR FILL (WET BULB TEMP=356K,
      APPROX. 50% RH AT 324K)
0940: PROPANE, PROPENE INJECTED

T=0 AT 1130 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.526	0.132	PPT
TS	DORIC-1	50.7	1.2	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.427	PPM
NO2-UNC	B-NOX-1	0.055	PPM
PROPANE	DMS-1	0.0127	PPM
PROPENE	DMS-1	0.0111	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
4600	B-NOX-1	BENDIX NOX ANALYZER MDB101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1050	-40	------	------	0.0132	0.0114	0.1480	------	------	------	------	------
1 1108	-22	------	------	0.0129	0.0112	0.1340	------	------	------	------	------
1 1110	-20	0.424	0.055	------	------	------	------	48.5	------	------	------
1 1122	-8	0.423	0.055	------	------	------	------	49.7	------	------	------
1 1130	0	0.427	0.055	0.0127	0.0111	0.1240	0.739	49.2	0.39	0.012	0.00302
1 1145	15	0.403	0.083	0.0126	0.0077	0.4840	0.682	50.4	------	------	------
1 1200	30	0.373	0.104	0.0122	0.0054	0.8160	0.538	50.6	------	------	------
1 1215	45	0.357	0.120	0.0122	0.0041	1.078	0.511	51.0	------	------	------
1 1230	60	0.336	0.134	0.0117	0.0031	1.327	0.548	51.2	------	------	------
1 1245	75	0.320	0.146	0.0117	0.0024	1.594	0.388	51.4	------	------	------
1 1300	90	0.302	0.154	0.0115	0.0019	1.783	0.427	51.8	------	------	------
1 1315	105	0.283	0.166	0.0108	0.0015	1.991	0.378	52.1	------	------	------
1 1330	120	0.266	0.172	0.0112	0.0013	2.175	------	52.3	0.64	0.017	0.00837

------ NO DATA TAKEN

EC-449
NOX-AIR, T=324K, DRY
1980 OCT. 15

0909: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0928: BEGIN FILL WITH LIQUID N2 EVAPORATE TO APPROX. 590 TORR.
0945: COMPLETE FILL WITH LIQUID O2 EVAPORATE
      PROPANE, PROPENE INJECTED

T=0 AT 1045 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.213	0.029	PPT
TS	DORIC-1	37.6	0.8	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.458	PPM
NO2-UNC	T 14B-3	0.110	PPM
PROPANE	DMS-1	0.0553	PPM
PROPENE	DMS-1	0.0112	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	FN-1	RM 121; POROPAK N ; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM FN-1	ETHENE PPM FN-1	ETHANE PPM FN-1	ACETYLEN PPM FN-1
1 1019	-26	-----	-----	0.0549	0.0110	1.753	-----	-----	-----	0.0000	0.0919	0.0000
1 1032	-13	-----	-----	0.0547	0.0112	1.734	-----	-----	7.32	-----	-----	-----
1 1045	0	0.458	0.110	0.0553	0.0112	1.742	0.248	-----	-----	-----	-----	-----
1 1048	3	-----	-----	-----	-----	-----	-----	37.5	-----	-----	-----	-----
1 1100	15	0.456	0.104	0.0555	0.0100	1.863	0.248	36.6	-----	-----	-----	-----
1 1115	30	0.454	0.104	0.0546	0.0087	1.984	0.168	36.6	-----	-----	-----	-----
1 1130	45	0.450	0.102	0.0541	0.0079	2.066	0.191	37.2	-----	-----	-----	-----
1 1145	60	0.445	0.109	0.0548	0.0073	2.159	0.238	37.8	-----	-----	-----	-----
1 1200	75	0.441	0.104	0.0547	0.0065	2.275	0.199	38.1	-----	-----	-----	-----
1 1215	90	0.438	0.106	0.0530	0.0057	2.372	0.205	38.2	-----	-----	-----	-----
1 1230	105	0.435	0.106	0.0530	0.0052	2.472	0.201	37.9	7.46	0.0003	0.0952	0.0001
1 1245	120	0.427	0.109	0.0531	0.0047	2.570	-----	38.9	-----	-----	-----	-----

----- = NO DATA TAKEN

161

EC-449
NOX-AIR, T=324K, DRY
1980 OCT. 15

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	BENZENE PPM 10'C-600	MEK PPM 10'C-600	ACETALD PPM 10'C-600	PROFALD PPM 10'C-600	ACETONE PPM 10'C-600	TOLUENE PPM 10'C-600
1 1019	-26	0.0021	0.003	0.0000	------	0.00065	------	0.0006	0.001
1 1245	120	0.0020	0.003	------	0.0001	0.00472	0.0003	0.0037	0.000

------- NO DATA TAKEN

EC-450
NOX-AIR, T=424K, H2O SATURATED
1980 OCT. 16

0835: NO,NO2 INJECTED USING VACUUM TECHNIQUE
0850: APPROX. 270 ML LIQUID H2O DRAWN INTO CHAMBER
0855: BEGIN DRY PURE AIR FILL
0926: PROPENE, PROPANE INJECTED
      FILL HALTED AT 650 TORR
1100: FILL COMPLETED

T=0 AT 1200 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.729	0.540	PPT
TS	DORIC-1	51.2	1.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.597	PPM
NO2-UNC	T 14B-3	0.140	PPM
PROPANE	DMS-1	0.0138	PPM
PROPENE	DMS-1	0.0123	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1116	-44	------	------	0.0142	0.0126	0.2670	------	------	------	------	------
1 1131	-29	------	------	0.0140	0.0125	0.2590	------	------	------	------	------
1 1158	-2	0.595	0.130	------	------	------	------	48.4	------	------	------
1 1200	0	0.597	0.140	0.0138	0.0123	0.2680	1.875	48.9	1.28	0.012	0.00407
1 1215	15	0.575	0.245	0.0130	0.0046	1.181	1.080	51.2	------	------	------
1 1230	30	0.567	0.271	0.0126	0.0026	1.707	0.832	51.4	------	------	------
1 1245	45	0.563	0.269	0.0123	0.0017	2.112	0.616	51.5	------	------	------
1 1300	60	0.553	0.265	0.0120	0.0012	2.412	0.421	51.8	------	------	------
1 1315	75	0.538	0.258	0.0121	0.0010	2.617	0.454	51.9	------	------	------
1 1330	90	0.530	0.247	0.0116	0.0008	2.838	0.265	52.2	------	------	------
1 1345	105	0.508	0.249	0.0115	0.0007	2.967	0.290	52.5	1.55	0.019	0.00935
1 1400	120	0.496	0.245	0.0115	0.0006	3.108	------	52.5	------	------	------

------ NO DATA TAKEN

EC-451
NOX-AIR, T=324K, HIGH NO2/NO
1980 OCT. 17

0922: NO, NO2 INJECTED USING VACUUM TECHNIQUE.
0936: BEGIN PURE AIR FILL (APPROX. 50% AT 324K)
0949: INJECT PROPANE, PROPENE.

T=0 AT 1130 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.428	0.235	PPT
TS	DORIC-1	52.2	0.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.148	PPM
NO2-UNC	T 14B-3	0.241	PPM
PROPANE	DMS-1	0.0137	PPM
PROPENE	DMS-1	0.0111	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1054	-36	------	------	0.0141	0.0114	0.2130	------	------	------	------	------
1 1100	-30	0.130	0.271	------	------	------	------	52.1	------	------	------
1 1108	-22	------	------	0.0138	0.0111	0.2129	------	------	------	------	------
1 1115	-15	0.134	0.258	------	------	------	------	51.9	------	------	------
1 1130	0	0.148	0.241	0.0137	0.0111	0.2073	0.980	51.2	0.90	0.014	0.00786
1 1131	1	0.163	0.195	------	------	------	0.483	------	------	------	------
1 1145	15	0.162	0.225	0.0132	0.0067	0.6845	0.431	52.1	------	------	------
1 1200	30	0.162	0.221	0.0130	0.0052	0.9198	0.363	52.6	------	------	------
1 1215	45	0.158	0.217	0.0124	0.0040	1.129	0.296	52.9	------	------	------
1 1230	60	0.151	0.215	0.0128	0.0035	1.306	0.320	52.5	------	------	------
1 1245	75	0.146	0.213	0.0124	0.0029	1.441	0.277	52.2	------	------	------
1 1300	90	0.140	0.202	0.0124	0.0025	1.585	0.320	52.3	------	------	------
1 1315	105	0.136	0.199	0.0124	0.0022	1.741	0.277	52.5	------	0.018	0.00786
1 1330	120	0.128	0.198	0.0122	0.0019	1.876	------	52.3	1.18	------	------

------ NO DATA TAKEN

EC-452
NOX-AIR, T=284K, STANDARD
1980 OCT. 20

0823: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0906: PROPANE, PROPENE INJECTED

T=0 AT 1000 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.101	0.009	PPT
TS	DORIC-1	11.6	0.7	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.375	PPM
NO2-UNC	T 14B-3	0.091	PPM
PROPANE	DMS-1	0.0123	PPM
PROPENE	DMS-1	0.0097	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO FPM T 14B-3	NO2-UNC FPM T 14B-3	PROPANE FPM DMS-1	PROPENE FPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 930	-30	------	------	0.0122	0.0097	0.2260	------	------	------	------	------
1 943	-17	0.377	0.088	------	------	------	------	11.6	------	------	------
1 945	-15	------	------	0.0122	0.0096	0.2290	------	------	------	------	------
1 1000	0	0.375	0.091	0.0123	0.0097	0.2350	0.090	9.8	0.80	0.001	0.00131
1 1015	15	0.375	0.088	0.0123	0.0093	0.2790	0.088	12.4	------	------	------
1 1030	30	0.375	0.087	0.0121	0.0088	0.3220	0.103	11.9	------	------	------
1 1045	45	0.375	0.087	0.0120	0.0082	0.3720	0.111	11.7	------	------	------
1 1100	60	0.373	0.084	0.0121	0.0079	0.4260	0.111	11.6	------	------	------
1 1115	75	0.371	0.083	0.0119	0.0074	0.4800	0.099	11.7	------	------	------
1 1130	90	0.368	0.083	0.0120	0.0070	0.5280	0.109	11.9	------	------	------
1 1145	105	0.365	0.083	0.0121	0.0067	0.5810	------	11.6	0.85	0.002	0.00187

------ NO DATA TAKEN

NOTES

0

EC-453
NOX-AIR, T=284K, DRY
1980 OCT. 21

0843: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0856: BEGIN FILL WITH LIQUID N2 EVAPORATE TO APPROX. 590 TORR
0916: COMPLETE FILL WITH LIQUID O2 EVAPORATE
      PROFANE, PROPENE INJECTED

T=0 AT 1000 PDT

K1 = 0.407 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.078	0.015	PPT
TS	DORIC-1	10.9	1.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.403	PPM
NO2-UNC	T 14B-3	0.109	PPM
PROFANE	DMS-1	0.0851	PPM
PROPENE	DMS-1	0.0098	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4050	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 930	-30	------	------	0.0866	0.0099	2.169	------	------	------	------	------
1 945	-15	------	------	0.0849	0.0097	2.163	------	------	------	------	------
1 954	-6	0.401	0.106	------	------	------	------	9.0	------	------	------
1 956	-4	0.403	0.106	------	------	------	------	9.0	------	------	------
1 1000	0	0.403	0.109	0.0851	0.0098	2.154	0.088	9.0	0.73	0.001	0.00115
1 1015	15	0.403	0.100	0.0836	0.0093	2.197	0.076	11.3	------	------	------
1 1030	30	0.401	0.099	0.0866	0.0092	2.234	0.066	11.4	------	------	------
1 1045	45	0.399	0.096	0.0868	0.0090	2.266	0.064	11.9	------	------	------
1 1100	60	0.395	0.096	0.0853	0.0086	2.297	0.092	12.2	------	------	------
1 1115	75	0.395	0.099	0.0868	0.0083	2.342	0.099	11.7	------	------	------
1 1130	90	0.395	0.095	0.0874	0.0080	2.390	0.064	11.9	------	------	------
1 1145	105	0.387	0.096	0.0853	0.0076	2.421	------	12.0	0.80	0.002	0.00145

------ NO DATA TAKEN

166

EC-454
NOX-AIR, T=284K, H2O SATURATED
1980 OCT, 22

0835: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0740: BEGIN PURE AIR FILL (APPROX. 50% RH AT 284K)
0854: PROPANE, PROFENE INJECTED

T=0 AT 945 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.228	0.038	PPT
TS	DORIC-1	10.8	1.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.373	PPM
NO2-UNC	T 14B-3	0.081	PPM
PROPANE	DMS-1	0.0113	PPM
PROFENE	DMS-1	0.0103	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 915	-30	0.375	0.083	0.0118	0.0107	0.0930	------	11.3	------	------	------
1 928	-17	------	------	0.0117	0.0105	0.1030	------	------	------	------	------
1 930	-15	0.377	0.084	------	------	------	------	9.8	------	------	------
1 945	0	0.373	0.081	0.0113	0.0103	0.0940	0.211	8.2	3.48	0.007	0.00137
1 1000	15	0.373	0.081	0.0108	0.0088	0.1970	0.246	10.5	------	------	------
1 1015	30	0.369	0.081	0.0113	0.0082	0.3170	0.232	10.6	------	------	------
1 1030	45	0.365	0.081	0.0112	0.0073	0.4300	0.162	10.6	------	------	------
1 1045	60	0.357	0.077	0.0113	0.0068	0.5090	0.211	11.6	------	------	------
1 1100	75	0.356	0.077	0.0109	0.0059	0.6120	0.244	11.6	------	------	------
1 1115	90	0.352	0.079	0.0112	0.0054	0.7310	0.220	12.0	------	------	------
1 1130	105	0.350	0.077	0.0110	0.0047	0.8380	0.296	11.4	------	------	------
1 1145	120	0.342	0.077	0.0110	0.0041	0.9820	------	10.9	3.37	0.007	0.00275

------   NO DATA TAKEN

167

EC-455
NOX-AIR, T=284K, HIGH NO2/NO
1980 OCT. 23

0715: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0832: BEGIN PURE AIR FILL (APPROX. 50% RH AT 284K)
0845: PROFANE, PROFENE INJECTED

T=0 AT 930 PDT

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.123	0.042	PPT
TS	DORIC-1	10.3	1.0	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.120	PPM
NO2-UNC	T 14B-3	0.360	PPM
PROFANE	DMS-1	0.0118	PPM
PROFENE	DMS-1	0.0101	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 900	-30	------	------	0.0122	0.0105	0.2950	------	------	------	------	------
1 915	-15	------	------	0.0117	0.0102	0.2840	------	------	------	------	------
1 916	-14	0.113	0.369	------	------	------	------	9.1	------	------	------
1 930	0	0.120	0.360	0.0118	0.0101	0.3000	0.201	8.0	------	------	------
1 931	1	0.147	0.347	------	------	------	------	------	2.62	0.026	0.00239
1 945	15	0.160	0.304	0.0115	0.0090	0.3980	0.152	10.4	------	------	------
1 1000	30	0.166	0.287	0.0117	0.0085	0.4720	0.119	10.2	------	------	------
1 1015	45	0.173	0.276	0.0115	0.0078	0.5300	0.113	10.5	------	------	------
1 1030	60	0.177	0.266	0.0117	0.0076	0.5850	0.113	10.8	------	------	------
1 1045	75	0.181	0.254	0.0118	0.0072	0.6400	0.119	10.9	------	------	------
1 1100	90	0.187	0.251	0.0115	0.0067	0.6980	0.053	10.9	------	------	------
1 1115	105	0.191	0.239	0.0115	0.0065	0.7240	0.111	11.0	------	------	------
1 1130	120	0.194	0.231	0.0113	0.0060	0.7780	------	11.2	2.68	0.003	0.00223

------ NO DATA TAKEN

EC-457
NOX-AIR, LIGHT INTENSITY VARIED

0816: NO, NO2 INJECTED USING VACUUM TECHNIQUE.
0833: BEGIN APPROX. 50% RH PURE AIR FILL
0833: PROPANE, PROPENE INJECTED
0950: BEGIN IRRADIATION, FULL INTENSITY, K1=0.49 MIN-1
1130: REDUCE IRRADIATION POWER, K1=0.25 MIN-1

T=0 AT 930 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	30.1	0.8	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.403	PPM
NO2-UNC	T 14B-3	0.093	PPM
PROPANE	DMS-1	0.0129	PPM
PROPENE	DMS-1	0.0099	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	FN-1	RM 121; POROPAK N ; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1
1 900	-30	------	------	------	------	------	------	------	1.45	0.0005	0.0018
1 930	0	0.403	0.093	0.0129	0.0099	0.2580	0.152	28.7	------	------	------
1 945	15	0.399	0.091	0.0125	0.0090	0.3320	0.166	29.3	------	------	------
1 1000	30	0.397	0.091	0.0125	0.0083	0.4130	0.185	29.6	------	------	------
1 1015	45	0.393	0.091	0.0126	0.0076	0.5030	0.170	30.2	------	------	------
1 1030	60	0.391	0.092	0.0123	0.0069	0.5860	0.189	30.9	------	------	------
1 1045	75	0.387	0.095	0.0123	0.0062	0.6780	0.187	31.1	------	------	------
1 1100	90	0.382	0.092	0.0123	0.0057	0.7690	0.197	31.2	------	------	------
1 1115	105	0.375	0.091	0.0123	0.0052	0.8650	0.164	31.5	------	------	------
1 1130	120	0.371	0.095	0.0121	0.0047	0.9460	0.121	31.5	1.42	0.0006	0.0017
1 1145	135	0.364	0.099	0.0121	0.0044	1.005	0.086	29.8	------	------	------
1 1200	150	0.361	0.100	0.0119	0.0042	1.047	0.072	29.6	------	------	------
1 1215	165	0.356	0.100	0.0117	0.0040	1.082	0.156	29.5	------	------	------
1 1230	180	0.352	0.102	0.0118	0.0037	1.158	0.103	29.5	------	------	------
1 1245	195	0.350	0.099	0.0117	0.0035	1.208	0.152	29.8	------	------	------
1 1300	210	0.343	0.100	0.0118	0.0033	1.282	0.105	29.8	------	------	------
1 1315	225	0.342	0.102	0.0117	0.0031	1.333	0.090	29.8	------	------	------
1 1330	240	0.338	0.100	0.0117	0.0029	1.377	------	29.8	1.44	0.0004	0.0015

------ NO DATA TAKEN

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EC-457
NOX-AIR, LIGHT INTENSITY VARIED

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM PN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	BENZENE PPM 10'C-600	MEK PPM 10'C-600	ACETALD PPM 10'C-600	PROFALD PPM 10'C-600	ACETONE PPM 10'C-600
1 900	-30	0.0003	0.0003	0.0009	0.001	0.0002	0.0004	0.0012	0.0002	0.0006
1 1130	120	0.0003	0.0004	0.0009	0.001	0.0001	------	0.0044	0.0002	0.0020
1 1330	240	0.0004	0.0003	0.0009	0.001	0.0001	------	0.0040	0.0002	0.0032

------ NO DATA TAKEN

EC-458
NOX-AIR, VARIABLE LIGHT INTENSITY
1980 OCT. 28

0844: NO, NO2 INJECTED USING VACUUM TECHNIQUE
0900: BEGIN APPROX. 50% RH PURE AIR FILL
0911: PROPANE, PROPENE INJECTED.
1000: LIGHTS ON WITH HALF LIGHT INTENSITY, K1=0.25 MIN-1
1200: IRRADIATION POWER INCREASED. K1=0.49 MIN-1

T=0 AT 1000 PDT

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	29.6	0.3	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.405	PPM
NO2-UNC	T 14B-3	0.083	PPM
PROFANE	DMS-1	0.0125	PPM
PROFENE	DMS-1	0.0109	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 930	-30	------	------	0.0127	0.0110	0.1360	------	------	------	------
1 945	-15	------	------	0.0128	0.0111	0.1390	------	------	------	------
1 952	-8	0.405	0.088	------	------	------	------	30.2	------	------
1 953	-7	0.407	0.087	------	------	------	------	30.2	------	------
1 1000	0	0.405	0.083	0.0125	0.0109	0.1360	0.062	29.2	0.009	0.00026
1 1015	15	0.403	0.081	0.0121	0.0103	0.1660	0.094	29.0	------	------
1 1030	30	0.401	0.083	0.0121	0.0098	0.2120	0.109	29.2	------	------
1 1045	45	0.395	0.081	0.0124	0.0095	0.2650	0.099	29.5	------	------
1 1100	60	0.393	0.079	0.0123	0.0089	0.3130	0.117	29.3	------	------
1 1115	75	0.387	0.079	0.0123	0.0085	0.3700	0.092	29.5	------	------
1 1130	90	0.387	0.079	0.0122	0.0080	0.4150	0.119	29.6	------	------
1 1145	105	0.386	0.079	0.0120	0.0074	0.4710	0.119	29.6	------	------
1 1200	120	0.379	0.081	0.0121	0.0071	0.5290	0.166	29.6	0.015	0.00378
1 1215	135	0.371	0.077	0.0121	0.0066	0.6100	0.228	29.8	------	------
1 1230	150	0.368	0.079	0.0119	0.0057	0.7210	0.189	29.4	------	------
1 1245	165	0.364	0.081	0.0107	0.0047	0.8130	0.209	29.4	------	------
1 1300	180	0.360	0.081	0.0117	0.0047	0.9150	0.234	29.5	------	------
1 1315	195	0.356	0.087	0.0117	0.0042	1.029	0.175	29.5	------	------
1 1330	210	0.347	0.081	0.0115	0.0038	1.114	0.172	29.9	------	------
1 1345	225	0.342	0.087	0.0094	0.0028	1.198	0.263	29.9	------	------
1 1400	240	0.338	0.087	0.0115	0.0030	1.326	------	30.1	------	0.00379

------ NO DATA TAKEN

171

EC-459
NOX-AIR, SYRINGE INJECTED NOX
1980 OCT. 29

0900: BEGIN APPROX. 50% RH PURE AIR FILL.
0920: PROPANE, PROPENE NO, NO2 INJECTED USING SYRINGE TECHNIQUE
      (THROUGH TEFLON DISPENSER TUBE)

T=0 AT 1000 PST

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.204	0.014	PPT
TS	DORIC-1	30.1	0.5	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.354	PPM
NO2-UNC	T 14B-3	0.100	PPM
PROPANE	DMS-1	0.0124	PPM
PROPENE	DMS-1	0.0116	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 930	-30	------	------	0.0124	0.0117	0.0570	------	------	------	------	------
1 945	-15	------	------	0.0124	0.0117	0.0550	------	------	------	------	------
1 947	-13	0.350	0.100	------	------	------	------	30.3	------	------	------
1 953	-7	0.352	0.100	------	------	------	------	30.2	------	------	------
1 1000	0	0.354	0.100	0.0124	0.0116	0.0620	0.201	29.1	0.22	0.012	0.00052
1 1015	15	0.356	0.096	0.0123	0.0104	0.1600	0.201	29.5	------	------	------
1 1030	30	0.354	0.095	0.0120	0.0092	0.2580	0.189	29.6	------	------	------
1 1045	45	0.352	0.092	0.0121	0.0086	0.3500	0.216	30.0	------	------	------
1 1100	60	0.352	0.091	0.0120	0.0077	0.4550	0.209	30.5	------	------	------
1 1115	75	0.347	0.091	0.0120	0.0069	0.5570	0.189	30.2	------	------	------
1 1130	90	0.339	0.088	0.0119	0.0062	0.6490	0.230	30.2	------	------	------
1 1145	105	0.342	0.088	0.0119	0.0055	0.7610	0.195	30.5	------	------	------
1 1200	120	0.334	0.088	0.0118	0.0050	0.8560	------	30.6	0.31	0.016	0.00399

------ NO DATA TAKEN

EC-460
NOX-AIR, NO INJECTION PREVIOUS DAY
1980 OCT. 31

OCT 30
0850: NO INJECTON USING VACUUM TECHNIQUE, NO2 NOT INJECTED.
0853: BEGIN APPROX. 50% RH PURE AIR FILL.
0912: FILL COMPLETE.
OCT 31
1135: PROPANE, PROPENE INJECTED.

T=0 AT 1245 PST

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.295	0.087	PPT
TS	DORIC-1	29.2	0.3	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.409	PPM
NO2-UNC	T 14B-3	0.063	PPM
PROPANE	DMS-1	0.0116	PPM
PROPENE	DMS-1	0.0105	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

EC-460
NOX-AIR, NO INJECTION PREVIOUS DAY
1980 OCT. 31

DY HR.	CLOCK TIME HR.	ELAPSED TIME (MIN)	NO PPM T14B-3	NO2-UNC PPM T14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1	1154	-51	------	------	0.0116	0.0107	0.2320	------	------	------	------	------
1	1210	-35	------	------	0.0117	0.0106	0.2450	------	------	------	------	------
1	1241	-4	0.408	0.067	------	------	------	0.448	------	0.40	0.022	0.00357
1	1245	0	0.409	0.063	0.0116	0.0105	0.2460	0.361	------	------	------	------
1	1300	15	0.391	0.075	0.0115	0.0084	0.4640	0.329	------	------	------	------
1	1315	30	0.374	0.085	0.0112	0.0069	0.6000	0.306	------	------	------	------
1	1330	45	0.365	0.089	0.0112	0.0059	0.8000	0.271	29.1	------	------	------
1	1345	60	0.356	0.092	0.0111	0.0050	0.9490	0.207	29.6	------	------	------
1	1400	75	0.347	0.100	0.0108	0.0044	1.081	0.261	29.1	------	------	------
1	1415	90	0.338	0.101	0.0110	0.0038	1.182	0.177	29.1	------	------	------
1	1430	105	0.330	0.104	0.0110	0.0035	1.309	------	29.1	------	------	------
1	1445	120	0.323	0.104	0.0108	0.0031	1.395	------	------	0.54	0.027	0.00568

------ NO DATA TAKEN

EC-462
NOX-AIR, O3 INJECTION
1980 NOV. 5

0845: NO, NO2 INJECTED USING VACUUM TECHNIQUE.
0900: BEGIN APPROX. 50% RH PURE AIR FILL.
0909: PROPANE, PROPENE INJECTED
1000: LIGHTS ON
1200: 100 ML APPROX. 2% O3 FLUSHED INTO CHAMBER

T=0 AT 1000 PST

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	31.4	1.7	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.409	PPM
NO2-UNC	T 14B-3	0.096	PPM
PROPANE	DMS-1	0.0110	PPM
PROPENE	DMS-1	0.0104	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 930	-30	----	----	0.0108	0.0100	0.0680	----	----	----	----	----
1 945	-15	0.411	0.099	0.0109	0.0104	0.0490	----	----	----	----	----
1 1000	0	0.409	0.096	0.0110	0.0104	0.0530	0.140	30.2	4.57	0.035	0.00869
1 1015	15	0.401	0.096	0.0111	0.0098	0.1210	0.163	29.9	----	----	----
1 1030	30	0.395	0.099	0.0108	0.0091	0.1710	----	30.3	----	----	----
1 1045	45	0.387	0.099	0.0108	0.0079	0.2800	0.193	29.8	----	----	----
1 1100	60	0.379	0.104	0.0108	0.0074	0.3740	0.090	30.0	----	----	----
1 1115	75	0.369	0.109	0.0107	0.0070	0.4180	0.179	30.6	----	----	----
1 1130	90	0.364	0.110	0.0105	0.0063	0.5050	0.152	30.9	----	----	----
1 1145	105	0.361	0.114	0.0106	0.0059	0.5790	0.187	30.6	----	----	----
1 1200	120	0.356	0.117	0.0108	0.0055	0.6700	0.152	30.9	4.67	0.019	0.02234
1 1215	135	0.168	0.288	0.0108	0.0051	0.7440	0.162	30.4	----	----	----
1 1230	150	0.169	0.280	0.0106	0.0047	0.8230	0.160	31.3	----	----	----
1 1245	165	0.173	0.271	0.0108	0.0044	0.9010	0.116	31.4	----	----	----
1 1300	180	0.173	0.262	0.0107	----	----	----	32.1	----	----	----
1 1315	195	0.177	0.254	0.0106	0.0038	1.014	0.205	32.9	----	----	----
1 1330	210	0.173	0.245	0.0105	0.0034	1.114	0.140	33.9	----	----	----
1 1345	225	0.172	0.239	0.0101	0.0031	1.182	0.043	34.8	----	----	----
1 1400	240	0.176	0.235	0.0101	0.0030	1.203	----	35.3	----	----	----

------ NO DATA TAKEN

EC-463
NOX-AIR, VARIED REACTANT INJECTION.
1980,NOV 6

0835: NO INJECTED USING VACUUM TECHNIQUE, NO2 NOT INJECTED.
0840: BEGIN APPROX. 50% RH PURE AIR FILL.
0903: PROFANE, PROFENE INJECTED.
1010: 100 ML APPROX. 2% O3 FLUSHED INTO CHAMBER.
1015: LIGHTS ON.
1216: APPROX. 0.16 PPM NO2 FLUSHED INTO CHAMBER.

T=0 AT 1015 PST

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	29.5	1.2	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.326	PPM
NO2-UNC	T 14B-3	0.172	PPM
PROFANE	DMS-1	0.0115	PPM
PROFENE	DMS-1	0.0115	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROFANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 920	-55	-----	-----	0.0118	0.0120	-0.0220	-----	-----	-----	-----	-----
1 937	-38	-----	-----	0.0120	0.0119	0.0080	-----	-----	-----	-----	-----
1 950	-25	-----	-----	0.0118	0.0116	0.0090	-----	-----	-----	-----	-----
1 1014	-1	0.328	0.176	------	------	-0.0080	0.088	26.2	2.84	0.016	-----
1 1015	0	0.326	0.172	0.0115	0.0115	0.0350	0.099	26.5	-----	-----	-----
1 1030	15	0.328	0.168	0.0120	0.0115	0.0830	0.133	29.3	-----	-----	-----
1 1045	30	0.326	0.160	0.0118	0.0109	0.1480	0.146	29.6	-----	-----	-----
1 1100	45	0.324	0.154	0.0124	0.0106	0.2190	0.090	29.5	-----	-----	-----
1 1115	60	0.324	0.156	0.0124	0.0099	0.2630	0.150	30.0	-----	-----	-----
1 1130	75	0.320	0.150	0.0120	0.0092	0.3360	0.045	29.9	-----	-----	-----
1 1145	90	0.316	0.146	0.0119	0.0084	0.3580	0.216	29.8	-----	-----	-----
1 1200	105	0.314	0.150	0.0113	0.0079	0.4630	0.066	30.0	-----	-----	-----
1 1215	120	0.310	0.146	0.0115	0.0072	0.4950	0.170	29.6	-----	-----	-----
1 1230	135	0.324	0.288	0.0105	0.0064	0.5780	0.119	29.8	-----	-----	-----
1 1245	150	0.324	0.276	0.0113	0.0063	0.6360	0.111	30.3	-----	-----	-----
1 1300	165	0.328	0.266	0.0113	0.0060	0.6900	0.121	30.2	-----	-----	-----
1 1315	180	0.330	0.261	0.0114	0.0057	0.7490	0.094	30.3	-----	-----	-----
1 1330	195	0.330	0.253	0.0115	0.0054	0.7950	0.082	30.3	-----	-----	-----
1 1345	210	0.330	0.241	0.0112	0.0050	0.8350	-----	30.2	3.07	0.016	0.00037
1 1400	225	0.326	0.231	0.0113	0.0049	-----	-----	30.3	-----	-----	-----
1 1415	240	-----	-----	0.0112	------	-----	-----	-----	-----	-----	-----

------- NO DATA TAKEN

176

EC-464
NOX-AIR, NO=NO2=0.1
1980, NOV 7

1000: NO,NO2 INJECTED USING VACUUM TECHNIQUE.
1007: BEGIN APPROX. 50% RH PURE AIR FILL.
1019: PROFANE, PROPENE INJECTED.

T=0 AT 1100 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.204	0.043	PPT
TS	DORIC-1	30.5	0.7	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.100	PPM
NO2-UNC	T 14B-3	0.093	PPM
PROFANE	DMS-1	0.0124	PPM
PROPENE	DMS-1	0.0110	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1
1 1030	-30	-----	-----	0.0123	0.0110	-----	-----	-----	2.42	0.0021	0.0065
1 1045	-15	-----	-----	0.0124	0.0111	-----	-----	-----	-----	-----	-----
1 1056	-4	0.100	0.092	-----	-----	-----	-----	-----	-----	-----	-----
1 1100	0	0.100	0.093	0.0124	0.0110	0.2640	0.302	29.3	-----	-----	-----
1 1115	15	0.106	0.084	0.0124	0.0095	0.4110	0.216	29.9	-----	-----	-----
1 1130	30	0.102	0.084	0.0122	0.0084	0.5160	0.205	29.6	-----	-----	-----
1 1145	45	0.099	0.084	0.0121	0.0076	0.6160	0.177	30.2	-----	-----	-----
1 1200	60	0.095	0.084	0.0122	0.0070	0.7020	0.185	30.7	-----	-----	-----
1 1215	75	0.092	0.087	0.0119	0.0063	0.7920	0.185	30.9	-----	-----	-----
1 1230	90	0.088	0.088	0.0118	0.0057	0.8820	0.162	31.0	-----	-----	-----
1 1245	105	0.083	0.091	0.0119	0.0053	0.9610	0.201	31.2	-----	-----	-----
1 1300	120	0.082	0.091	0.0117	0.0047	1.059	-----	31.2	2.43	0.0019	0.0068

----- = NO DATA TAKEN

177

EC-464
NOX-AIR, NO=NO2=0.1
1980, NOV 7

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM FN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	MEK PPM 10'C-600	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1030	-30	0.0038	0.0038	0.0009	0.001	------	0.0007	------	0.0009
1 1300	120	------	0.0039	------	------	0.0000	0.0030	0.0002	0.0026

------ NO DATA TAKEN

EC-465
NOX-AIR, NO=NO2=0.4
1980, NOV 12

0846: NO,NO2 INJECTED USING VACUUM TECHNIQUE.
0859: BEGIN PURE AIR FILL, 50% RH.
0910: PROPANE, PROFENE INJECTED.

T=0 AT 1000 PST

K1 = 0.487 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.117	0.033	PPT
TS	DORIC-1	29.5	0.6	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.399	PPM
NO2-UNC	T 14B-3	0.371	PPM
PROPANE	DMS-1	0.0124	PPM
PROFENE	DMS-1	0.0109	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 927	-33	0.397	0.373	0.0121	0.0111	0.9483	------	29.2	------	------	------
1 942	-18	------	------	0.0123	0.0109	0.9768	------	------	------	------	------
1 947	-13	0.399	0.373	------	------	------	------	29.3	------	------	------
1 958	-2	0.401	0.369	------	------	------	------	28.7	------	------	------
1 1000	0	0.399	0.371	0.0124	0.0109	0.9875	0.186	28.4	1.13	0.002	0.00209
1 1015	15	0.411	0.342	0.0124	0.0100	1.078	0.129	29.2	------	------	------
1 1030	30	0.421	0.322	0.0121	0.0092	1.141	0.095	29.3	------	------	------
1 1045	45	0.428	0.312	0.0122	0.0088	1.188	0.120	29.6	------	------	------
1 1100	60	0.437	0.298	0.0120	0.0082	1.246	0.092	30.0	------	------	------
1 1115	75	0.441	0.287	0.0120	0.0078	1.291	0.087	30.0	------	------	------
1 1130	90	0.445	0.276	0.0115	0.0072	1.334	0.129	30.2	------	------	------
1 1145	105	0.449	0.265	0.0118	0.0069	1.397	0.097	30.2	------	------	------
1 1200	120	0.449	0.258	0.0118	0.0066	1.444	------	30.2	1.23	0.015	0.00328

------ = NO DATA TAKEN

EC-469
NOX-AIR, DEFOCUSED LIGHT.
1980,NOV 18

DEFOCUSED LIGHT SOURCE USED
1000: NO, NO2 INJECTED USING VACUUM TECHNIQUE.
1017: BEGIN APPROX. 50% RH PURE AIR FILL.
1026: PROPENE AND PROPANE INJECTED.
1130: BEGIN IRRADIATION, HALF LIGHT INTENSITY, K1=0.25 MIN-1
1328: IRRADIATION POWER INCREASED, K1=0.50 MIN-1

T=0 AT 1130 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	30.0	1.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-3	0.399	PPM
NO2-UNC	T 14B-3	0.104	PPM
PROPANE	DMS-2	0.0095	PPM
PROPENE	DMS-2	0.0086	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID
1530	T 14B-3	TECO 14B-3 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-3	NO2-UNC PPM T 14B-3	PROPANE PPM DMS-2	PROPENE PPM DMS-2	LNC3/C3*	HYDROXYL PPT	TS DEG C DORIC-1	CO PPM BK6800-1	HCHO PPM CA	ACETALD PPM 10'C-600
1 1040	-50	------	------	0.0096	0.0136	------	------	------	------	------	------
1 1102	-28	------	------	0.0094	0.0097	------	------	------	------	------	------
1 1115	-15	0.401	0.104	0.0095	0.0088	0.0670	0.047	27.6	------	------	------
1 1130	0	0.399	0.104	0.0095	0.0086	0.0900	0.140	28.8	0.42	0.010	------
1 1145	15	0.395	0.102	0.0094	0.0080	0.1600	0.101	29.0	------	------	------
1 1200	30	0.391	0.100	0.0094	0.0076	0.2090	0.064	29.2	------	------	------
1 1215	45	0.383	0.102	0.0094	0.0074	0.2400	0.084	29.6	------	------	------
1 1230	60	0.382	0.102	0.0091	0.0049	0.2810	0.092	29.6	------	------	------
1 1245	75	0.377	0.104	0.0091	0.0066	0.3260	0.086	29.8	------	------	------
1 1300	90	0.373	0.106	0.0094	0.0065	0.3680	0.097	30.0	------	------	------
1 1315	105	0.371	0.106	0.0092	0.0061	0.4150	0.105	30.2	------	------	0.06570
1 1326	116	------	------	------	------	------	------	------	------	------	------
1 1330	120	0.368	0.104	0.0090	0.0057	0.4660	0.181	32.0	------	------	------
1 1345	135	0.360	0.110	0.0092	0.0053	0.5540	0.177	31.5	------	------	------
1 1400	150	0.354	0.113	0.0090	0.0048	0.6400	0.152	30.6	------	------	------
1 1415	165	0.343	0.106	0.0089	0.0043	0.7140	0.164	30.3	------	------	------
1 1430	180	0.339	0.113	0.0090	0.0041	0.7940	0.168	30.7	------	------	------
1 1445	195	0.334	0.114	0.0091	0.0038	0.8760	0.136	31.0	------	------	------
1 1500	210	0.324	0.113	0.0089	0.0035	0.9420	------	30.7	0.43	0.017	------

------ NO DATA TAKEN

AFF- 11
NOX - AIR IRRADIATION (NEW BAG)
1980 JULY 11

NEW BAG # 15 INSTALLED
0932: 4 ML NO2 INJECTED
0934: 17 ML NO INJECTED
0953: .8 ML PROPANE ADDED
1007: .8 ML PROPENE INJECTED
1048: BAG UNCOVERED.
WEATHER CLEAR AND HOT,
NO OZONE FORMATION OCCURED

BAG FILLED WITH APPROXIMATELY 50% R. H. PURE AIR

T=0 AT 1048 PST

BAG NO.   15 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.079	0.039	PPT
TS	DORIC-1	39.2	2.9	DEG C
K1		0.406	0.046	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.485	PPM
NO2-UNC	B-NOX-1	0.124	PPM
PROPANE	DMS-1	0.1840	PPM
PROPENE	DMS-1	0.1780	PPM

INSTRUMENTS USED

ID.	LABEL	DESCRIPTION
4300	TSI 023	TSI ELECTRICAL AEROSOL ANALYZER MD:3030
4400	MRI 388	MRI INTEGRATING NEPHELOMETER MD:1550B
4900	B-03-1	BENDIX O3 ANALYZER MD5513340-X SN32787-5
1790	D-1790	DASIBI 1790 OZONE MONITOR
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2920	10'C-600	RM-121; 10', 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4350	CLIMET	CLIMET OPC MD:208 SN76-148
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER

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AFF- 11
NOX - AIR IRRADIATION (NEW BAG)
1980 JULY 11

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-1
1 850	-118	-----	-----	-----	0.0045	0.0017	0.9734	-----	-----	-----	-----	2.16
1 903	-105	0.025	0.010	0.033	0.0183	0.0178	0.0277	-----	34.1	-----	-----	2.16
1 1026	-22	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1033	-15	0.485	0.124	0.605	0.0184	0.0178	0.0332	-----	35.5	-----	-----	-----
1 1038	-10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1100	12	0.453	0.127	0.575	0.0198	0.0186	0.0625	0.087	37.0	0.411 A	3.92	2.47
1 1103	15	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1115	27	0.437	0.127	0.555	0.0201	0.0181	0.1048	0.067	38.5	0.405	3.90	2.67
1 1118	30	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1130	42	0.430	0.123	0.545	0.0195	0.0170	0.1372	0.054	40.0	0.366	3.54	2.88
1 1133	45	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1145	57	0.447	0.130	0.570	0.0199	0.0169	0.1634	0.146	40.2	0.477	4.64	2.88
1 1148	60	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1200	72	0.420	0.130	0.540	0.0196	0.0155	0.2347	0.027	41.0	0.380	3.70	3.19
1 1203	75	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1215	87	0.410	0.133	0.535	0.0196	0.0153	0.2477	0.068	41.5	0.457	4.44	3.29
1 1218	90	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1230	102	0.402	0.139	0.530	0.0196	0.0148	0.2809	0.106	41.9	0.412	3.99	3.50
1 1233	105	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1245	117	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1248	120	0.393	0.144	0.525	0.0198	0.0142	0.3324	-----	42.8	0.338	3.25	3.60

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC PPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM FN-1	ETHENE PPM FN-1	ETHANE PPM FN-1	ACETYLEN PPM PN-1	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600	TOLUENE PPM 10'C-600	#PART>.3 PART/CC CLIMET
1 850	-118	-----	-----	-----	-----	-----	-----	0.021	0.0011	0.0026	0.002	-----
1 903	-105	2.73	1.83	-----	-----	-----	-----	-----	-----	-----	-----	3.
1 907	-101	-----	-----	2.08	0.0439	0.0081	0.0076	-----	-----	-----	-----	-----
1 1033	-15	2.64	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1103	15	2.64	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1118	30	2.64	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1133	45	2.64	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1148	60	2.73	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1203	75	2.64	1.79	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1218	90	2.64	1.79	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1233	105	2.73	1.83	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1248	120	2.69	1.79	2.07	0.0358	0.0068	0.0046	0.014	0.0005	0.0014	0.010	-----

----- NO DATA TAKEN

AFF- 11
NOX - AIR IRRADIATION (NEW BAG)
1980 JULY 11

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	#PART>.5 PART/CC CLIMET	#PART>1 PART/CC CLIMET	BSCAT 10-4 M-1 MRI 388	AER.V UM3/CC TSI 023	AER.N PART/CC TSI 023	AER.S UM2/CC TSI 023	PART.024 PART/CC TSI 023	PART.042 PART/CC TSI 023	PART.075 PART/CC TSI 023	PART.133 PART/CC TSI 023	PART.237 PART/CC TSI 023
1 903	-105	0.	0.	0.5	18.	3.5E 04	577.	1.9E 04	5394.	6083.	3808.	652.
1 1033	-15	----	0.	0.3	4.	1.1E 04	145.	6680.	1305.	1510.	1012.	172.
1 1103	15	----	----	----	----	----	----	----	----	----	----	----
1 1118	30	----	----	----	----	----	----	----	----	----	----	----
1 1133	45	----	----	----	----	----	----	----	----	----	----	----
1 1148	60	----	----	----	----	----	----	----	----	----	----	----
1 1203	75	----	----	----	----	----	----	----	----	----	----	----
1 1218	90	----	----	----	----	----	----	----	----	----	----	----
1 1233	105	----	----	----	----	----	----	----	----	----	----	----
1 1248	120	----	----	----	----	----	----	----	----	----	----	----

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	PART.422 PART/CC TSI 023	PART.750 PART/CC TSI 023
1 903	-105	87.	18.
1 1033	-15	0.	7.

------ NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

1029: 5 ML NO2 INJECTED
1031: 15 ML NO INJECTED
1033: 0.6 ML PROPANE ADDED
1035: 0.6 ML PROPENE ADDED
1111: BAG DIVIDED
1145: BAG UNCOVERED
NO OZONE FORMATION OCCURED.
BAG FILLED WITH 50% R. H. PURE AIR.

T=0 AT 1145 PST

BAG NO.   16 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS	
HYDROXYL		0.095	0.006	PPT	SIDE 1
HYDROXYL		0.072	0.021	PPT	SIDE 2
TS	DORIC-1	40.8	2.8	DEG C	SIDE 1
TS	DORIC-1	41.2	2.8	DEG C	SIDE 2
K1		0.342	0.032	MIN-1	SIDE 1
K1		0.359	0.031	MIN-1	SIDE 2

ID	INST.	INITIAL CONC.	UNITS	
NO	BENDIX	0.461	PPM	SIDE 1
NO	BENDIX	0.461	PPM	SIDE 2
NO2-UNC	BENDIX	0.138	PPM	SIDE 1
NO2-UNC	BENDIX	0.138	PPM	SIDE 2
PROPANE	DMS-1	0.0231	PPM	SIDE 1
PROPANE	DMS-1	0.0231	PPM	SIDE 2
PROPENE	DMS-1	0.0186	PPM	SIDE 1
PROPENE	DMS-1	0.0186	PPM	SIDE 2

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2100	FN-1	RM 121; POROPAK N ; FID
1790	D-1790	DASIBI 1790 OZONE MONITOR
1700	BENDIX	AF-LAB BENDIX NO-NOX NYLON FILT ANALYZER
1600	BK6800-2	BECKMAN HYDROCARBON GC MD:6800 SN:100016
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4300	TSI 023	TSI ELECTRICAL AEROSOL ANALYZER MD:3030
4400	MRI 388	MRI INTEGRATING NEPHELOMETER MD:1550B
4200	CNC-143	ENV. ONE CNC MD:RICH100, SN:143
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2750	SE-52C-2	RM-121; 30M SE-52 QUARTZ CAPILLARY; FID
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
4350	CLIMET	CLIMET OPC MD:208 SN76-148
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS

AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 NO PPM BENDIX	SIDE 2 NO PPM BENDIX	SIDE 1 NO2-UNC PPM BENDIX	SIDE 2 NO2-UNC PPM BENDIX	SIDE 1 NOX-UNC PPM BENDIX	SIDE 2 NOX-UNC PPM BENDIX	SIDE 1 PROPANE PPM DMS-1	SIDE 2 PROPANE PPM DMS-1	SIDE 1 PROPENE PPM DMS-1	SIDE 2 PROPENE PPM DMS-1
1 933	-132	---	---	---	---	---	---	0.0064	0.0064	0.0010	0.0010
1 940	-125	---	---	---	---	---	---	0.0238	0.0238	0.0188	0.0188
1 1045	-60	0.479	---	0.139	---	0.598	---	0.0264	---	0.0208	---
1 1115	-30	---	0.461	---	0.138	---	0.580	---	---	---	---
1 1125	-20	---	---	---	---	---	---	---	---	---	---
1 1126	-19	---	---	---	---	---	---	---	0.0231	---	0.0186
1 1155	10	---	0.451	---	0.143	---	0.580	0.0230	---	0.0175	---
1 1204	19	0.447	---	0.142	---	0.580	---	---	---	---	---
1 1205	20	---	---	---	---	---	---	---	---	---	---
1 1215	30	---	0.438	---	0.152	---	0.575	---	---	---	---
1 1218	33	0.433	---	0.157	---	0.576	---	---	0.0235	---	0.0170
1 1225	40	---	0.423	---	0.159	---	0.572	---	---	---	---
1 1235	50	0.417	---	0.163	---	0.568	---	---	---	---	---
1 1245	60	---	0.414	---	0.162	---	0.562	---	---	---	---
1 1255	70	---	---	---	---	---	---	---	---	---	---
1 1304	79	---	---	---	---	---	---	0.0232	---	0.0145	---
1 1305	80	0.400	---	0.171	---	0.560	---	---	---	---	---
1 1315	90	---	0.397	---	0.171	---	0.556	---	---	---	---
1 1325	100	0.387	---	0.178	---	0.556	---	---	---	---	---
1 1327	102	---	---	---	---	---	---	---	0.0223 A	---	0.0129 A
1 1335	110	---	0.383	---	0.177	---	0.546	---	---	---	---
1 1345	120	0.366	---	0.190	---	0.550	---	---	---	---	---
1 1355	130	---	0.363	---	0.190	---	0.544	---	---	---	---
1 1404	139	---	---	---	---	---	---	0.0221 A	---	0.0116 A	---
1 1405	140	0.352	---	0.197	---	0.544	---	---	---	---	---
1 1415	150	---	0.349	---	0.193	---	0.536	---	---	---	---
1 1419	154	---	---	---	---	---	---	---	0.0213 A	---	0.0113 A
1 1500	195	---	---	---	---	---	---	0.0224 B	---	0.0099 B	---
1 1515	210	---	---	---	---	---	---	---	0.0213 B	---	0.0099 B

------   NO DATA TAKEN

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AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

CLOCK TIME DY	HR.	ELAPSED TIME (MIN)	SIDE 1 LNC3/C3=	SIDE 2 LNC3/C3=	SIDE 1 HYDROXYL PPT	SIDE 2 HYDROXYL PPT	SIDE 1 TS DEG C DORIC-1	SIDE 2 TS DEG C DORIC-1	SIDE 1 K1 MIN-1	SIDE 2 K1 MIN-1	SIDE 1 UV .MW/CM2 EPPLEY	SIDE 2 UV MW/CM2 EPPLEY
1	933	-132										
1	940	-125										
1	1045	-60	0.2358	0.2358			34.8	34.8				
1	1115	-30	0.2384					39.1				
1	1125	-20					38.2					
1	1126	-19		0.2167		0.063				0.340 D		3.23 C
1	1155	10						39.1				
1	1204	19	0.2733						0.345 D		3.28 C	
1	1205	20			0.101		40.0					
1	1215	30				0.100		41.8		0.371		3.52
1	1218	33		0.3238			40.9					
1	1225	40							0.353	0.378	3.34	3.57
1	1235	50						42.4				
1	1245	60					41.8		0.341	0.401	3.20	3.74
1	1255	70						42.3				
1	1304	79	0.4700									
1	1305	80			0.090		42.5		0.325	0.352	3.01	3.23
1	1315	90						44.0	0.392		3.56	
1	1325	100		0.5474			43.0					
1	1327	102				0.051						
1	1335	110						42.8	0.353	0.388	3.12	3.48
1	1345	120					42.7					
1	1355	130						42.6		0.312		2.72
1	1404	139	0.6446						0.286		2.45	
1	1405	140			0.095		43.0					
1	1415	150				0.073		43.0		0.330		2.78
1	1419	154		0.6339								
1	1500	195	0.8165									
1	1515	210		0.7662								

------ NO DATA TAKEN

AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 CO PPM BK6800-2	SIDE 2 CO PPM BK6800-2	SIDE 1 THC FPMC BK6800-2	SIDE 2 THC FPMC BK6800-2	METHANE PPM PN-1	SIDE 1 METHANE PPM BK6800-2	SIDE 2 METHANE PPM BK6800-2	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	HCHO PPM CA
1 933	-132	------	------	------	------	2.13	------	------	0.0059	0.0105	0.0072	------
1 940	-125	1.56	1.56	1.94	1.94	------	1.93	1.93	------	------	------	------
1 1100	-45	------	------	------	------	------	1.91	------	------	------	------	0.002
1 1115	-30	1.44	1.62	2.04	1.95	------	------	1.90	------	------	------	------
1 1125	-20	------	1.56	------	2.03	------	------	1.90	------	------	------	------
1 1155	10	------	------	------	------	------	------	------	------	------	------	------
1 1205	20	1.56	1.56	2.00	1.97	------	1.91	1.90	------	------	------	------
1 1215	30	------	------	------	------	------	1.90	------	------	------	------	------
1 1225	40	1.55	1.56	1.96	1.92	------	------	1.89	------	------	------	------
1 1235	50	------	------	------	------	------	1.92	------	------	------	------	------
1 1245	60	1.60	1.57	1.90	1.99	------	------	1.91	------	------	------	------
1 1255	70	------	------	------	------	------	1.88	------	------	------	------	------
1 1305	80	1.53	1.61	1.96	1.95	------	------	1.94	------	------	------	------
1 1315	90	------	------	------	------	------	1.80	------	------	------	------	------
1 1325	100	1.60	1.58	0.87	1.02	------	------	1.92	------	------	------	------
1 1335	110	------	------	------	------	------	1.77	------	------	------	------	------
1 1345	120	1.61	1.58	1.79	1.42	------	------	1.77	------	------	------	------
1 1355	130	------	------	------	------	------	1.80	------	------	------	------	------
1 1405	140	1.59	------	1.77	------	------	------	1.80	------	------	------	------
1 1415	150	------	1.36	------	1.77	------	------	------	------	------	------	------

------ NO DATA TAKEN

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AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETALD PPM 10'C-600	SIDE 1 AER.V UM3/CC TSI 023	SIDE 2 AER.V UM3/CC TSI 023	SIDE 1 AER.N PART/CC TSI 023	SIDE 2 AER.N PART/CC TSI 023	SIDE 1 AER.S UM2/CC TSI 023	SIDE 2 AER.S UM2/CC TSI 023	SIDE 1 PART.024 PART/CC TSI 023	SIDE 2 PART.024 PART/CC TSI 023	SIDE 1 PART.042 PART/CC TSI 023	SIDE 2 PART.042 PART/CC TSI 023
1 940	-125	----	-0.	----	110.	----	4.	----	0.	----	-87.	----
1 955	-110	0.018	----	-0.	----	110.	----	4.	----	0.	----	-87.
1 1115	-30	----	1.	----	145.	----	4.	----	167.	----	-87.	----
1 1125	-20	----	----	0.	----	362.	----	4.	----	334.	----	-174.
1 1155	10	----	1.	----	65.	----	5.	----	0.	----	0.	----
1 1205	20	----	----	1.	----	227.	----	9.	----	167.	----	0.
1 1215	30	----	1.	----	862.	----	14.	----	501.	----	87.	----
1 1225	40	----	----	2.	----	-127.	----	14.	----	-167.	----	0.
1 1235	50	----	1.	----	1712.	----	25.	----	-668.	----	1740.	----
1 1245	60	----	----	-0.	----	57.	----	4.	----	-835.	----	696.
1 1255	70	----	1.	----	1917.	----	43.	----	-668.	----	1218.	----
1 1305	80	----	----	0.	----	596.	----	10.	----	334.	----	0.
1 1315	90	----	1.	----	3248.	----	39.	----	835.	----	783.	----
1 1325	100	----	----	-0.	----	461.	----	5.	----	0.	----	87.
1 1335	110	----	1.	----	3206.	----	54.	----	334.	----	783.	----
1 1345	120	----	----	0.	----	988.	----	11.	----	0.	----	609.
1 1355	130	----	1.	----	3240.	----	65.	----	167.	----	609.	----
1 1405	140	----	----	0.	----	1199.	----	14.	----	167.	----	522.
1 1415	150	----	----	1.	----	1075.	----	24.	----	-167.	----	609.

------ NO DATA TAKEN

AFF- 24
NOX - AIR IRRADIATION
1980 AUG 8

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PART.075 PART/CC TSI 023	SIDE 2 PART.075 PART/CC TSI 023	SIDE 1 PART.133 PART/CC TSI 023	SIDE 2 PART.133 PART/CC TSI 023	SIDE 1 PART.237 PART/CC TSI 023	SIDE 2 PART.237 PART/CC TSI 023	SIDE 1 PART.422 PART/CC TSI 023	SIDE 2 PART.422 PART/CC TSI 023	SIDE 1 PART.750 PART/CC TSI 023	SIDE 2 PART.750 PART/CC TSI 023
1 940	-125	133.	133.	48.	48.	12.	12.	7.	7.	-4.	-4.
1 1115	-30	44.	----	24.	----	0.	----	-7.	----	4.	----
1 1125	-20	----	178.	----	24.	----	0.	----	0.	----	0.
1 1155	10	----	44.	24.	0.	0.	12.	-7.	0.	4.	4.
1 1205	20	44.	----	----	----	----	----	----	----	----	----
1 1215	30	----	44.	----	-24.	----	12.	----	0.	----	7.
1 1225	40	222.	----	48.	----	0.	----	0.	----	4.	----
1 1235	50	----	133.	----	72.	----	-12.	----	7.	----	-4.
1 1245	60	577.	----	48.	----	25.	----	-13.	----	4.	----
1 1255	70	----	178.	289.	72.	12.	12.	0.	0.	4.	0.
1 1305	80	1066.	----	----	----	----	----	----	----	----	----
1 1315	90	----	311.	120.	72.	0.	-12.	0.	7.	0.	-4.
1 1325	100	1510.	----	----	----	----	----	----	----	----	----
1 1335	110	----	355.	313.	24.	0.	0.	0.	0.	0.	0.
1 1345	120	1776.	----	----	----	----	----	----	----	----	----
1 1355	130	----	444.	410.	48.	12.	25.	0.	-7.	0.	0.
1 1405	140	2042.	----	----	----	----	----	----	----	----	----
1 1415	150	----	533.	----	96.	----	0.	----	0.	----	4.

------   NO DATA TAKEN

NOTES

A   SOMETHING WAS WRONG WITH THE RETENTION TIMES; CARRIER GAS FLOW WAS
    INCORRECT

B   CARRIER FLOW HAS BEEN RESET TO CORRECT VALUE FOR THOSE LAST TWO SAMPLES.

C   EPPLEY UV RADIOMETER PLACED UNDER BAG ON SIDE BEING SAMPLED

D   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 27
NOX-AIR IRRADIATION
1980 AUG 21

1231: 0.8 ML PROPANE INJECTED
1233: 0.8 ML PROPENE INJECTED
1235: 5 ML NO2 ADDED
1237: 17 ML NO ADDED
1300: BAG UNCOVERED
NO OZONE FORMATION OCCURRED.
BAG FILLED WITH APPROXIMATELY 30 % R. H. PURE AIR.

T=0 AT 1300 PST

BAG NO.   17 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.039	0.044	PPT
TS	DORIC-1	35.8	0.6	DEG C
K1		0.322	0.086	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	BENDIX	0.283	PPM
NO2-UNC	BENDIX	0.092	PPM
PROPANE	DMS-1	0.0327	PPM
PROPENE	DMS-1	0.0331	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1790	D-1790	DASIBI 1790 OZONE MONITOR
1700	BENDIX	AF-LAB BENDIX NO-NOX NYLON FILT ANALYZER
1600	BK6800-2	BECKMAN HYDROCARBON GC MD;6800 SN:100016
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID

AFF- 27
NOX-AIR IRRADIATION
1980 AUG 21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM BENDIX	NO2-UNC PPM BENDIX	NOX-UNC PPM BENDIX	PROPANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-2
1 1252	-8	-----	-----	-----	0.0327	0.0331	-0.0103	-----	-----	-----	-----	-----
1 1255	-5	0.283	0.092	0.380	-----	-----	-----	-----	36.0	0.400 A	3.65	2.06
1 1310	10	0.282	0.093	0.380	-----	-----	-----	-----	36.0	0.394	3.55	2.16
1 1315	15	-----	-----	-----	0.0334	0.0335	-0.0024	0.087	-----	-----	-----	-----
1 1320	20	0.282	0.091	0.378	-----	-----	-----	-----	36.1	0.324	2.89	2.20
1 1330	30	0.280	0.091	0.377	0.0324	0.0311	0.0399	-0.007	36.4	0.343	3.02	2.24
1 1340	40	0.279	0.092	0.372	-----	-----	-----	-----	36.5	0.459	3.99	2.35
1 1345	45	-----	-----	-----	0.0312	0.0300	0.0365	0.108	-----	-----	-----	-----
1 1350	50	0.279	0.092	0.376	-----	-----	-----	-----	36.0	0.255	2.18	2.39
1 1400	60	0.279	0.092	0.372	0.0333	0.0304	0.0890	0.023	36.5	0.435	3.66	2.41
1 1410	70	0.277	0.092	0.370	-----	-----	-----	-----	36.0	0.257	2.12	2.48
1 1415	75	-----	-----	-----	0.0338	0.0306	0.1000	0.051	-----	-----	-----	-----
1 1420	80	0.278	0.093	0.372	-----	-----	-----	-----	35.8	0.211	1.71	2.44
1 1430	90	0.276	0.093	0.372	0.0333	0.0294	0.1247	0.006	35.5	0.335	2.64	2.56
1 1440	100	0.272	0.094	0.371	-----	-----	-----	-----	35.2	0.195	1.49	2.56
1 1445	105	-----	-----	-----	0.0327	0.0288	0.1279	0.005	-----	-----	-----	-----
1 1450	110	0.271	0.095	0.370	-----	-----	-----	-----	34.8	0.337	2.51	2.60
1 1500	120	0.272	0.097	0.371	0.0336	0.0295	0.1301	-----	35.0	0.238	1.72	2.68

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC PPHC BK6800-2	METHANE PPM PN-1	METHANE PPM BK6800-2	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	ACETALD PPM 10'C-600
1 1252	-8	-----	2.31	2.03	-----	-----	-----	0.020
1 1255	-5	2.04	-----	2.03	-----	-----	-----	-----
1 1310	10	1.94	-----	2.03	-----	-----	-----	-----
1 1320	20	1.98	-----	2.01	-----	-----	-----	-----
1 1330	30	1.99	-----	2.03	A	A	A	-----
1 1340	40	1.96	-----	2.04	-----	-----	-----	-----
1 1350	50	1.92	-----	2.04	-----	-----	-----	-----
1 1400	60	1.82	-----	2.02	-----	-----	-----	-----
1 1410	70	2.11	-----	2.00	-----	-----	-----	-----
1 1420	80	1.87	-----	2.02	-----	-----	-----	-----
1 1430	90	1.96	-----	2.03	-----	-----	-----	-----
1 1440	100	1.94	-----	2.01	-----	-----	-----	-----
1 1450	110	2.01	-----	2.01	-----	-----	-----	-----
1 1500	120	1.97	2.28	2.01	0.0054	0.0107	0.0052	0.014

----- NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 35
NOX - AIR IRRADIATION
1980 SEP 11

0902: 6 ML NO2 INJECTED
0904: 18 ML NO INJECTED
0906: 0.8 ML PROPANE ADDED
0908: 0.8 ML PROPENE ADDED
1000: BAG UNCOVERED
NO OZONE FORMATION OCCURED
BAG FILLED WITH APPROXIMATELY 25% R. H. PURE AIR.

T=0 AT 1000 PST

BAG NO. 17 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.043	0.047	PPT
TS	DORIC-1	26.4	3.0	DEG C
K1		0.363	0.009	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.402	PPM
NO2-UNC	B-NOX-1	0.146	PPM
PROPANE	DMS-1	0.0235	PPM
PROPENE	DMS-1	0.019	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID

AFF- 35
NOX - AIR IRRADIATION
1980 SEP 11

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3= PN-1	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-1
1 944	-16	-----	-----	-----	0.0236	0.019	0.2136	-----	-----	-----	-----	-----
1 950	-10	0.401	0.146	0.539	-----	-----	-----	-----	22.0	0.353 A	2.76	2.02
1 1000	0	0.402	0.146	0.539	0.0235	0.019	0.2037	0.068	22.2	0.344	2.76	1.96
1 1010	10	0.399	0.146	0.539	0.0241	0.019	0.2368	0.108	22.9	-----	-----	1.90
1 1015	15	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1020	20	0.399	0.142	0.536	0.0240	0.018	0.2894	-0.048	23.8	0.352	2.87	1.92
1 1030	30	0.398	0.147	0.536	0.0237	0.018	0.2660	0.040	24.6	0.365	3.02	1.80
1 1040	40	0.393	0.146	0.537	-----	-----	-----	-----	25.4	0.368	3.09	1.95
1 1045	45	-----	-----	-----	0.0234	0.018	0.2853	0.053	-----	-----	-----	-----
1 1050	50	0.393	0.144	0.534	0.0238	0.018	0.3110	0.029	26.1	0.364	3.09	1.95
1 1100	60	0.396	0.149	0.536	-----	-----	-----	-----	26.8	0.365	3.13	1.93
1 1110	70	0.393	0.144	0.534	0.0238	0.017	0.3251	0.079	27.8	0.371	3.21	1.99
1 1115	75	-----	-----	-----	0.0238	0.017	-----	-----	-----	-----	-----	-----
1 1120	80	0.390	0.147	0.536	0.0239	0.017	0.3635	0.017	28.8	0.369	3.21	1.88
1 1130	90	0.389	0.147	0.530	-----	-----	-----	-----	28.9	0.370	3.24	1.91
1 1140	100	0.387	0.149	0.532	0.0239	0.017	-----	-----	29.6	0.366	3.21	1.95
1 1145	105	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1150	110	0.387	0.150	0.534	-----	-----	-----	-----	30.2	0.371	3.26	1.96
1 1200	120	0.386	0.149	0.528	0.0239	0.016	0.3719	-----	30.5	0.356	3.13	1.97

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC FPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM PN-1	ETHANE PPM PN-1	ETHENE PPM FN-1	ACETYLEN PPM PN-1	BENZENE PPM 10'C-600	MEK PPM 10'C-600	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600	TOLUENE PPM 10'C-600
1 944	-16	-----	-----	2.42	0.0127	0.0103	0.0116	0.0002	0.0001	0.003	0.0010	0.000
1 950	-10	1.97	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1000	0	2.27	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1010	10	1.93	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1020	20	1.95	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1030	30	1.92	2.10	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1040	40	2.00	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1050	50	2.02	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1100	60	1.96	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1110	70	1.98	2.11	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1120	80	1.93	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1130	90	2.00	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1140	100	1.96	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1150	110	1.94	2.12	-----	-----	-----	-----	-----	-----	-----	-----	-----
1 1200	120	2.02	2.12	2.39	0.0130	0.0109	0.0153	0.0001	-----	0.007	0.0014	-----

-----   NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 41
NOX IRRADIATION
1980 OCT 1

1038: INJECT 6.0 ML NO2
1040: INJECT 18.0 ML NO
1042: .4 ML PROPENE AND .4 ML PROPANE ADDED
1120: BAG UNCOVERED
NO OZONE FORMATION OCCURRED.
BAG FILLED WITH 43% R. H. PURE AIR.

T=0 AT 1120 PST

BAG NO. 18 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.043	0.066	PPT
TS	DORIC-1	43.3	1.0	DEG C
K1		0.338	0.027	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.398	PPM
NO2-UNC	B-NOX-1	0.139	PPM
PROPANE	DMS-1	0.0146	PPM
PROPENE	DMS-1	0.0106	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EFFLEY	ARB LAB; EFFLEY 11692 UV RADIOMETER
2100	FN-1	RM 121; POROPAK N ; FID
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS

AFF- 41
NOX IRRADIATION
1980 OCT 1

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-1
1 1110	-10	0.398	0.139	0.538	0.0146	0.0106	0.3145	----	41.3	----	----	1.74
1 1130	10	0.393	0.139	0.526	----	----	----	----	41.9	0.387 A	3.13	1.71
1 1135	15	----	----	----	0.0139	0.0097	0.3597	0.008	----	----	----	----
1 1140	20	0.392	0.139	0.526	----	----	----	----	41.9	0.377	3.06	1.76
1 1150	30	0.392	0.133	0.520	0.0133	0.0092	0.3635	0.145	43.0	0.363	2.95	1.72
1 1200	40	0.390	0.134	0.520	----	----	----	----	43.3	0.339	2.76	1.72
1 1205	45	----	----	----	0.0139	0.0090	0.4342	0.043	----	----	----	----
1 1210	50	0.391	0.137	0.521	----	----	----	----	43.4	0.343	2.79	1.70
1 1220	60	0.382	0.137	0.516	0.0138	0.0088	0.4553	0.034	43.7	0.340	2.76	1.77
1 1230	70	0.383	0.136	0.514	----	----	----	----	44.0	0.338	2.73	1.72
1 1235	75	----	----	----	0.0142	0.0089	0.4718	0.116	----	----	----	----
1 1240	80	0.387	0.137	0.516	----	----	----	----	44.1	0.320	2.57	1.81
1 1250	90	0.383	0.133	0.514	0.0141	0.0083	0.5281	-0.007	44.2	0.309	2.46	1.79
1 1300	100	0.383	0.131	0.514	----	----	----	----	44.2	0.313	2.46	1.79
1 1305	105	----	----	----	0.0139	0.0082	0.5248	-0.040	----	----	----	----
1 1310	110	0.383	0.131	0.514	----	----	----	----	44.1	0.317	2.46	1.78
1 1320	120	0.385	0.131	0.512	0.0120	0.0072	0.5054	----	44.2	0.307	2.35	1.79

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC FPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	HCHO PPM CA
1 1110	-10	1.35	1.79	1.80	0.0033	0.0065	0.0044	----
1 1120	0	----	----	----	----	----	----	0.025
1 1130	10	1.41	1.80	----	----	----	----	----
1 1140	20	1.36	1.81	----	----	----	----	----
1 1150	30	1.36	1.78	----	----	----	----	----
1 1200	40	1.35	1.79	----	----	----	----	----
1 1210	50	1.39	1.78	----	----	----	----	----
1 1220	60	1.37	1.80	----	----	----	----	----
1 1230	70	1.36	1.76	----	----	----	----	----
1 1240	80	1.38	1.77	----	----	----	----	----
1 1250	90	1.34	1.80	----	----	----	----	----
1 1300	100	1.36	1.78	----	----	----	----	----
1 1310	110	1.37	1.80	----	----	----	----	0.039
1 1320	120	1.33	1.79	1.76	0.0035	0.0069	0.0045	----

-----   NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 46
NOX IRRADIATION
1980, OCT 20

OCT 20

918: START FILL
1019: FILL ENDED
1022: RH DRY: 31.0 WET:12.2 RH=< 10%
1038-1040: INJECT 6.0 ML NO2
1040-1042: INJECT 18.0 ML NO
1042-1044: INJECT .4 ML C3, .4 ML C3=
1050: HCHO PRE T=0
1130: UNCOVER BAG
1135: WEATHER- EXTREMELY CLEAR, HOT; SANTA ANA CONDITIONS
1340: RUN OVER; BAG COVERED; BAG DUMPED
NO OZONE FORMATION OCCURRED.

T=0 AT 1130 PST

BAG NO. 18 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.048	0.061	PPT
TS	DORIC-1	31.8	1.1	DEG C
K1		0.370	0.025	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.369	PPM
NO2-UNC	B-NOX-1	0.147	PPM
PROPANE	DMS-1	0.0098	PPM
PROPENE	DMS-1	0.0084	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MDB101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
1600	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
2100	FN-1	RH 121; POROPAK N ; FID
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

AFF- 46
NOX IRRADIATION
1980, OCT 20

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EFFLEY	CO PPM BK6800-1
1 1030	-60	0.000	0.002	0.002	-----	-----	-----	-----	29.6	-----	-----	0.53
1 1109	-21	-----	-----	-----	0.0120	0.0095	0.2285	-----	-----	-----	-----	-----
1 1110	-20	0.369	0.147	0.514	0.0098	0.0084	0.1594	-----	30.3	-----	-----	0.55
1 1130	0	0.370	0.143	0.514	-----	-----	-----	0.144	-----	-----	-----	-----
1 1140	10	-----	-----	-----	0.0117	0.0093	0.2297	0.059	30.4	0.397 A	2.91	0.56
1 1145	15	0.368	0.140	0.504	-----	-----	-----	-----	-----	-----	-----	-----
1 1150	20	0.371	0.143	0.512	0.0118	0.0091	0.2585	-----	31.4	0.388	2.85	0.55
1 1200	30	0.372	0.139	0.506	0.0115	0.0088	0.2633	0.010	31.4	0.400	2.94	0.64
1 1210	40	-----	-----	-----	-----	-----	-----	-----	32.5	0.377	2.77	0.53
1 1215	45	0.370	0.140	0.506	-----	-----	-----	-----	-----	-----	-----	-----
1 1220	50	0.369	0.139	0.504	0.0106	0.0081	0.2649	0.003	32.4	0.389	2.85	0.47
1 1230	60	0.369	0.138	0.504	-----	-----	-----	0.119	32.4	0.381	2.78	0.58
1 1240	70	-----	-----	-----	0.0086	0.0062	0.3226	-0.007	32.2	0.370	2.68	0.61
1 1245	75	0.370	0.140	0.504	-----	-----	-----	-----	-----	-----	-----	-----
1 1250	80	0.367	0.137	0.500	-----	-----	-----	0.076	32.8	0.363	2.61	0.58
1 1300	90	0.364	0.138	0.500	0.0102	0.0074	0.3191	-----	32.3	0.378	2.69	0.56
1 1310	100	-----	-----	-----	-----	-----	-----	-----	32.8	0.342	2.41	0.52
1 1315	105	0.366	0.135	0.500	0.0105	0.0073	0.3559	-0.019	-----	-----	-----	-----
1 1320	110	0.368	0.133	0.500	-----	-----	-----	-----	32.8	0.337	2.34	0.54
1 1330	120	-----	-----	-----	0.0113	0.0080	0.3467	-----	32.5	0.320	2.19	-----

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC PPMC BK6800-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	BENZENE PPM 10'C-600	ACETALD PPM 10'C-600
1 1030	-60	1.22	1.63	-----	-----	-----	-----	-----
1 1109	-21	-----	-----	0.0018	0.0021	0.0014	0.0001	0.005
1 1110	-20	1.35	1.62	-----	-----	-----	-----	-----
1 1140	10	1.24	1.61	-----	-----	-----	-----	-----
1 1150	20	1.22	1.61	-----	-----	-----	-----	-----
1 1200	30	1.18	1.63	-----	-----	-----	-----	-----
1 1210	40	1.25	1.61	-----	-----	-----	-----	-----
1 1220	50	1.19	1.61	-----	-----	-----	-----	-----
1 1230	60	1.25	1.62	-----	-----	-----	-----	-----
1 1240	70	1.24	1.62	-----	-----	-----	-----	-----
1 1250	80	1.19	1.60	-----	-----	-----	-----	-----
1 1300	90	1.24	1.61	-----	-----	-----	-----	-----
1 1310	100	1.20	1.58	-----	-----	-----	-----	-----
1 1320	110	1.22	1.60	-----	-----	-----	-----	-----
1 1330	120	-----	1.70	0.0015	0.0023	0.0024	0.0002	0.003

-----   NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 47
NOX IRRADIATION
1980, OCT 23

OCT 23
BAG FILLED WITH <10% RH PURE AIR.
1104: 6 ML NO2 INJECTED
1106: 18 ML NO INJECTED
1108: .4 ML EACH OF PROPANE AND PROPENE INJECTED
1130: UNCOVER BAG (T=0)
1340: RUN OVER
NO OZONE FORMATION OCCURRED.
BAG FILLED WITH DRY AIR.

T=0 AT 1130 PST

BAG NO.   19 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.023	0.130	PPT
TS	DORIC-1	33.6	1.2	DEG C
K1		0.318	0.043	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.394	PPM
NO2-UNC	B-NOX-1	0.144	PPM
PROPANE	DMS-1	0.0112	PPM
PROPENE	DMS-1	0.0091	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
1000	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

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AFF- 47
NOX IRRADIATION
1980, OCT 23

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL FPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-1
1 1120	-10	----	----	----	0.0112	0.0091	0.2045	----	----	----	----	----
1 1125	-5	0.394	0.144	0.538	----	----	----	----	31.4	----	----	2.13
1 1131	1	----	----	----	0.0106	0.0088	0.1952	0.226	----	----	----	----
1 1145	15	0.392	0.147	0.540	0.0100	0.0074	0.2981	-0.219	32.0	0.396 A	2.858	2.10
1 1200	30	0.393	0.141	0.538	0.0074	0.0061	0.1915	-0.082	33.4	0.343	2.481	2.29
1 1215	45	0.392	0.148	0.538	0.0105	0.0083	0.2316	0.094	33.4	0.338	2.439	2.30
1 1230	60	0.387	0.139	0.526	0.0112	0.0085	0.2774	0.018	33.9	0.328	2.370	2.32
1 1245	75	0.388	0.141	0.524	0.0110	0.0082	0.2861	-0.036	34.2	0.310	2.203	2.58
1 1300	90	0.388	0.139	0.524	0.0102	0.0078	0.2684	0.063	34.2	0.286	2.007	2.44
1 1315	105	0.388	0.137	0.524	0.0105	0.0078	0.2993	-0.047	34.3	0.274	1.889	2.70
1 1330	120	0.388	0.139	0.524	0.0107	0.0081	0.2764	----	35.2	0.268	1.812	2.60

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC PPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	BENZENE PPM 10'C-600	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1120	-10	----	----	1.95	0.002	0.0043	0.0011	0.0003	0.006	0.0019
1 1125	-5	1.23	1.85	----	----	----	----	----	----	----
1 1145	15	1.08	1.81	----	----	----	----	----	----	----
1 1200	30	1.22	1.84	----	----	----	----	----	----	----
1 1215	45	1.37	1.80	----	----	----	----	----	----	----
1 1230	60	1.21	1.81	----	----	----	----	----	----	----
1 1245	75	1.43	1.85	----	----	----	----	----	----	----
1 1300	90	1.34	1.80	----	----	----	----	----	----	----
1 1315	105	1.45	1.83	----	----	----	----	----	----	----
1 1330	120	1.40	1.80	1.93	0.008	0.0162	0.0038	0.0003	0.007	0.0022

------ NO DATA TAKEN

NOTES

A K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 51
NOX IRRADIATION
1980, OCT 30

OCT 30
BAG FILLED WITH <10% RH PURE AIR
1032: 6 ML NO2 INJECTED
1034: 18 ML NO INJECTED
1036: .4 ML EACH OF PROPANE AND PROPENE INJECTED
1145: UNCOVER BAG (T=0)
1150: TEFLON COVER PUT OVER FRAME
1155: WEATHER: CLEAR, WARM, SANTA ANA WINDS
1355: RUN OVER
NO OZONE FORMATION OCCURRED.

T=0 AT 1145 PST

DAG NO.   19 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.039	0.085	PPT
TS	DORIC-1	32.5	1.6	DEG C
K1		0.269	0.048	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.404	PPM
NO2-UNC	B-NOX-1	0.133	PPM
PROPANE	DMS-1	0.0106	PPM
PROPENE	DMS-1	0.0089	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

AFF- 51
NOX IRRADIATION
1980, OCT 30

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	UV RAD MW/CM2 EPPLEY	CO PPM BK6800-1
1 1050	-55	----	----	----	0.0112	0.0095	0.1631	----	----	----	----	----
1 1125	-20	0.404	0.133	0.532	----	----	----	----	29.5	----	----	0.36
1 1145	0	----	----	----	0.0106	0.0089	0.1750	0.023	----	----	----	----
1 1200	15	0.400	0.131	0.526	0.0115	0.0095	0.1863	-0.077	30.9	0.360 A	2.52	0.28
1 1215	30	0.401	0.131	0.524	0.0099	0.0085	0.1487	0.191	31.1	0.272	1.90	0.36
1 1230	45	0.399	0.131	0.522	0.0105	0.0083	0.2419	-0.001	32.7	0.309	2.15	0.35
1 1245	60	0.401	0.131	0.524	0.0102	0.0080	0.2564	0.031	33.0	0.272	1.87	0.38
1 1300	75	0.401	0.130	0.524	0.0100	0.0077	0.2357	-0.043	33.8	0.219	1.49	0.39
1 1315	90	0.399	0.126	0.522	0.0095	0.0075	0.2784	0.088	34.0	0.266	1.78	0.37
1 1330	105	0.399	0.131	0.521	0.0102	0.0077	0.3255	0.097	34.0	0.211	1.38	0.46
1 1345	120	0.399	0.129	0.518	0.0102	0.0074	----	----	33.6	0.243	1.56	0.39

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	THC PPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1	BENZENE PPM 10'C-600	ACETALD PPM 10'C-600
1 1050	-55	----	----	1.48	0.0017	0.0010	0.0003	----	----
1 1115	-30	----	----	----	----	----	----	0.0002	0.006
1 1125	-20	1.04	1.37	----	----	----	----	----	----
1 1200	15	1.08	1.48	----	----	----	----	----	----
1 1215	30	0.99	1.45	----	----	----	----	----	----
1 1230	45	1.00	1.48	----	----	----	----	----	----
1 1245	60	0.98	1.46	----	----	----	----	----	----
1 1300	75	0.99	1.48	----	----	----	----	----	----
1 1315	90	0.98	1.48	----	----	----	----	----	----
1 1330	105	1.02	1.47	----	----	----	----	----	----
1 1345	120	0.98	1.47	1.48	0.0010	0.0012	0.0004	0.0002	0.003

------ NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

AFF- 61
NOX - AIR IRRADIATION
1981 FEB. 3

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0821: FILLED BAG WITH 20% R.H. PURE AIR
0949: INJECT 6 ML. NO2
0951: INJECT 6 ML. NO
0953: INJECT 0.4 ML. PROPANE
0955: INJECT 0.4 ML. PROPENE
1030: START HCHO SAMPLE
1052: INJECTED 12.0 MORE ML. OF NO
      TO MAKE TOTAL NO=18.0 ML.
1115: UNCOVERED BAG (T=0)
1325: RUN OVER, BAG COVERED
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T=0 AT 1115 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.027	0.020	PPT
TS	DORIC-1	22.2	1.3	DEG C
K1		0.367	0.047	MIN-1

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.418	PPM
NO2-UNC	B-NOX-1	0.160	PPM
PROPANE	DMS-1	0.0110	PPM
PROPENE	DMS-1	0.0097	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER HD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
880	EG&G	EG&G DEW POINT HYGROMETER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
4130	EFFLEY	ARB LAB; EFFLEY 11692 UV RADIOMETER
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2100	FN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	OZONE PPM D-1790	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	NOX-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	K1 MIN-1	DEW PT DEG C EG&G
1 1045	-30	------	------	------	------	0.0117	0.0100	------	------	------	------	------
1 1105	-10	0.000	0.418	0.158	0.562	------	------	------	------	19.8	------	-1.5000
1 1108	-7	------	------	------	------	0.0110	0.0097	------	------	------	------	-1.5000 A
1 1115	0	0.000	0.418	0.160	0.564	------	------	0.1537	0.001	20.7	0.247	------
1 1130	15	0.001	0.417	0.160	0.564	0.0113	0.0097	0.1542	0.067	21.4	0.364	------
1 1145	30	0.000	0.419	0.159	0.564	0.0118	0.0098	0.1871	0.033	22.1	0.387	------
1 1200	45	0.001	0.418	0.159	0.562	0.0119	0.0097	0.2032	0.025	22.1	0.410	------
1 1215	60	0.001	0.415	0.156	0.560	0.0118	0.0095	0.2155	0.039	22.4	0.382	------
1 1230	75	0.001	0.416	0.153	0.561	0.0117	0.0093	0.2343	0.027	23.1	0.374	------
1 1245	90	0.002	0.418	0.153	0.561	0.0120	0.0094	0.2475	0.017	23.3	0.396	------
1 1300	105	0.001	0.417	0.152	0.560	0.0119	0.0092	0.2557	0.010	23.8	0.373	------
1 1315	120	0.001	0.417	0.151	0.558	0.0119	0.0092	0.2603	------	23.4	0.373	-1.5000

------ NO DATA TAKEN

AFF- 61
NOX - AIR IRRADIATION
1981 FEB. 3

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	UV RAD MW/CM2 EPPLEY	THC PPMC BK6800-1	METHANE PPM BK6800-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM DMS-1	ACETYLEN PPM PN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	CO PPM BK6800-1
1 1045	-30	-----	-----	-----	1.42	0.0024	0.0053	0.0018	0.0020	0.0009	0.0008	-----
1 1105	-10	-----	1.23	1.26	----	----	----	----	----	----	----	1.04
1 1115	0	1.66	1.41	1.24	----	----	----	----	----	----	----	1.07
1 1130	15	2.47	1.25	1.25	----	----	----	----	----	----	----	1.05
1 1145	30	2.64	1.24	1.27	----	----	----	----	----	----	----	1.15
1 1200	45	2.80	1.26	1.28	----	----	----	----	----	----	----	1.12
1 1215	60	2.61	1.24	1.28	----	----	----	----	----	----	----	1.15
1 1230	75	2.54	1.21	1.39	----	----	----	----	----	----	----	1.33
1 1245	90	2.66	1.19	1.28	----	----	----	----	----	----	----	1.18
1 1300	105	2.48	1.23	1.27	----	----	----	----	----	----	----	1.21
1 1315	120	2.44	1.20	1.36	1.39	0.0025	0.0061	0.0018	0.0019	0.0008	0.0009	1.21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1045	-30	0.00576	0.0000	0.0007
1 1315	120	0.00397	0.0002	0.0010

------ NO DATA TAKEN

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

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ITC-377
NOX-AIR IRRADIATION, NEW BAG.
1980 NOV. 21
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BAG FLUSHED AND FILLED 3 TIMES.
0900: BAG FILLED WITH APPROX. 50% RH PURE AIR.
0903: PROPANE AND PROPENE INJECTED.
0911: 2.4 ML. NO INJECTED, 0.6 ML. NO2 INJECTED.
0945: LIGHTS ON- 100%

T=0 AT 945 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.080	0.033	PPT
TS	DORIC-1	31.9	2.4	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.373	PPM
NO2-UNC	T 14B-1	0.114	PPM
PROPANE	DMS-1	0.0117	PPM
PROPENE	DMS-1	0.0108	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 927	-18	0.440	0.111	0.0114	0.0105	0.0820	------	25.5	1.68	0.0011	0.0033	0.0011
1 945	0	0.373	0.114	0.0117	0.0108	0.0809	0.188	25.5	------	------	------	------
1 1000	15	0.292	0.080	0.0093	0.0079	0.1726	0.082	30.9	------	------	------	------
1 1015	30	0.297	0.076	0.0095	0.0077	0.2127	0.078	31.7	------	------	------	------
1 1030	45	0.292	0.080	0.0095	0.0074	0.2506	0.077	32.1	------	------	------	------
1 1045	60	0.288	0.083	0.0095	0.0071	0.2882	0.072	32.6	------	------	------	------
1 1100	75	0.283	0.088	0.0095	0.0069	0.3235	0.070	32.8	------	------	------	------
1 1115	90	0.275	0.090	0.0095	0.0067	0.3575	0.080	32.9	------	------	------	------
1 1130	105	0.271	0.093	0.0095	0.0064	0.3964	0.100	33.0	------	------	------	------
1 1145	120	0.266	0.098	0.0092	0.0059	0.4451	0.030	32.9	------	------	------	------
1 1200	135	0.258	0.100	0.0093	0.0059	0.4598	0.098	33.0	------	------	------	------
1 1215	150	0.256	0.102	0.0094	0.0057	0.5074	0.078	33.0	------	------	------	------
1 1230	165	0.251	0.107	0.0095	0.0055	0.5452	0.064	33.0	------	------	------	------
1 1245	180	0.246	0.109	0.0094	0.0053	0.5763	0.085	32.9	------	------	------	------
1 1300	195	0.239	0.109	0.0095	0.0051	0.6175	0.068	32.9	------	------	------	------
1 1315	210	0.234	0.114	0.0094	0.0049	0.6507	0.047	32.9	------	------	------	------
1 1330	225	0.229	0.117	0.0092	0.0047	0.6738	0.070	33.0	1.66	0.0012	0.0029	0.0006
1 1345	240	0.224	0.119	0.0095	0.0047	0.7080	------	33.2				

------ NO DATA TAKEN

ITC-377
NOX-AIR IRRADIATION, NEW BAG.
1980 NOV. 21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	PROPALD PPM 10'C-600	ACETONE PPM 10'C-600
1 927	-18	0.0008	0.0011	0.00273	------	0.0010
1 1345	240	0.0008	0.0009	0.00865	0.0003	0.0009

------ NO DATA TAKEN

205

ITC-378
NOX-AIR IRRADIATION, REPEAT.
1980 NOV. 24

0900: BAG EXHAUSTED AND FILLED 2 TIMES.
0928: FINAL FILL- RH AT 300 DEGREES K DRY, AND 297 DEGREES K WET=APPROX. 50% RH
0928: PROPANE AND PROPENE INJECTED.
0933: NO AND NO2 INJECTED.
1030: LIGHTS ON- 100%, AIR HANDLER ON.
1114: TEMP. = 91.4 DEGREES F.

T=0 AT 1030 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL	DORIC-1	0.089	0.037	PPT
TS	DORIC-1	32.1	2.2	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.493	PPM
NO2-UNC	T 14B-1	0.119	PPM
PROPANE	DMS-1	0.0096	PPM
PROPENE	DMS-1	0.0082	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 950	-40	-----	-----	0.0097	0.0082	0.1651	------	------	1.57	0.0008	0.0027	0.0011
1 1007	-23	-----	-----	0.0098	0.0083	0.1715	------	------	-----	-----	-----	-----
1 1030	0	0.493	0.119	0.0096	0.0082	0.1554	0.153	26.5	-----	-----	-----	-----
1 1045	15	0.322	0.071	0.0096	0.0076	0.2298	0.128	31.5	-----	-----	-----	-----
1 1100	30	0.312	0.073	0.0099	0.0074	0.2923	0.092	32.6	-----	-----	-----	-----
1 1115	45	0.312	0.076	0.0099	0.0071	0.3372	0.058	33.0	-----	-----	-----	-----
1 1130	60	0.307	0.076	0.0098	0.0067	0.3654	0.099	33.0	-----	-----	-----	-----
1 1145	75	0.307	0.078	0.0096	0.0065	0.4134	0.070	33.0	-----	-----	-----	-----
1 1200	90	0.305	0.078	0.0096	0.0061	0.4473	0.064	33.0	-----	-----	-----	-----
1 1215	105	0.302	0.078	0.0097	0.0060	0.4782	0.048	33.2	1.56	0.0008	0.0027	0.0009
1 1230	120	0.302	0.078	0.0097	0.0059	0.5018	------	------	-----	-----	-----	-----

------ NO DATA TAKEN

ITC-378
NOX-AIR IRRADIATION, REPEAT,
1980 NOV. 24

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600
1 950	-40	0.0007	0.0009	0.00544	0.0011
1 1230	120	0.0008	0.0009	0.00566	0.0007

------ NO DATA TAKEN

ITC-379
NOX-AIR IRRADIATION, HIGH NO2/NO.
1980,NOV 24

BAG FLUSHED WITH 50% R.H. PURE AIR
NO, NO2, PROPANE, PROPENE INJECTED
1658: TEMP. = 92.2 DEGREES F.
1700: BAG DUMPED AND FILLED.

T=0 AT 1500 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.065	0.027	PPT
TS	DORIC-1	32.0	3.1	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.098	PPM
NO2-UNC	T 14B-1	0.222	PPM
PROPANE	DMS-1	0.0108	PPM
PROPENE	DMS-1	0.0089	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1
1 1427	-33	------	------	0.0105	0.0086	0.1981	------	------	------	------	------
1 1445	-15	------	------	------	------	------	------	------	1.59	0.0013	0.0034
1 1446	-14	------	------	0.0108	0.0087	0.2021	0.118	24.1	------	------	------
1 1500	0	0.098	0.222	0.0108	0.0089	------	------	------	------	------	------
1 1501	1	0.126	0.202	0.0106	0.0082	0.2596	0.068	30.5	------	------	------
1 1515	15	0.134	0.197	0.0107	0.0080	0.2928	0.060	32.0	------	------	------
1 1530	30	0.136	0.195	0.0106	0.0077	0.3221	0.049	32.8	------	------	------
1 1545	45	0.139	0.192	0.0108	0.0077	0.3460	0.042	33.4	------	------	------
1 1600	60	0.141	0.187	0.0106	0.0073	0.3664	0.059	33.6	------	------	------
1 1615	75	0.144	0.187	0.0108	0.0073	0.3950	0.086	33.7	------	------	------
1 1630	90	0.146	0.185	0.0110	0.0071	0.4371	0.034	33.9	------	------	------
1 1645	105	0.148	0.183	0.0108	0.0069	0.4535	------	33.7	------	------	------
1 1700	120	0.148	0.183	------	------	------	------	------	------	------	------

------ NO DATA TAKEN

208

ITC-379
NOX-AIR IRRADIATION, HIGH NO2/NO.
1980,NOV 24

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM PN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1427	-33	0.0012	------	0.0010	0.0012	------	------
1 1445	-15	------	0.0011	------	------	0.00222	------
1 1700	120	0.0012	------	0.0011	0.0012	0.00356	0.0003

------ NO DATA TAKEN

209

ITC-380
NOX-AIR IRRADIATON, VARIABLE LIGHT INTEN
1980,NOV 25

0830: FLUSH AND DUMP BAG 3 TIMES.
0912: INJECTIONS MADE DURING FINAL BAG
      FILL WITH ~50% R.H. PURE AIR USED
1000-1146 100% LIGHTS
1146-1246 80% LIGHTS
1246-1346 60% LIGHTS
1346-1446 40% LIGHTS
1446-1600 20% LIGHTS
1639: DUMP AND REFILL BAG.

T=0 AT 1000 PST

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	29.7	2.7	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.312	PPM
NO2-UNC	T 14B-1	0.073	PPM
PROPANE	DMS-1	0.0108	PPM
PROPENE	DMS-1	0.0087	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

ITC-380
NOX-AIR IRRADIATON, VARIABLE LIGHT INTEN
1980,NOV 25

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROFANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM FN-1	ETHENE PPM FN-1	ETHANE PPM FN-1
1 930	-30	0.305	0.071	0.0102	0.0086	------	------	27.6	1.65	0.0013	0.0033
1 945	-15	0.312	0.073	0.0104	0.0087	------	------	27.0	----	------	------
1 1000	0	0.312	0.073	0.0108	0.0087	0.2099	-0.012	27.2	----	------	------
1 1015	15	0.314	0.071	0.0102	0.0083	0.2041	0.083	31.7	----	------	------
1 1030	30	0.314	0.073	0.0102	0.0080	0.2447	0.064	32.6	----	------	------
1 1045	45	0.314	0.071	0.0104	0.0079	0.2758	0.054	33.3	----	------	------
1 1100	60	0.312	0.073	0.0101	0.0075	0.3022	0.082	33.7	----	------	------
1 1115	75	0.314	0.073	0.0104	0.0074	0.3422	0.087	33.2	----	------	------
1 1130	90	0.312	0.073	0.0105	0.0071	0.3846	0.024	33.0	----	------	------
1 1145	105	0.312	0.076	0.0105	0.0070	0.3965	0.034	33.2	----	------	------
1 1200	120	0.312	0.073	0.0105	0.0069	0.4130	0.091	32.1	----	------	------
1 1215	135	0.312	0.073	0.0106	0.0067	0.4572	0.019	31.8	----	------	------
1 1230	150	0.307	0.078	0.0102	0.0064	0.4662	0.068	31.7	----	------	------
1 1245	165	0.305	0.078	0.0104	0.0063	0.4995	0.055	31.7	----	------	------
1 1300	180	0.305	0.078	0.0105	0.0062	0.5265	-0.009	30.3	----	------	------
1 1315	195	0.302	0.078	0.0104	0.0062	0.5221	0.065	29.8	----	------	------
1 1330	210	0.302	0.078	0.0104	0.0060	0.5537	0.068	29.3	----	------	------
1 1345	225	0.300	0.080	0.0106	0.0059	0.5867	-0.026	29.6	----	------	------
1 1400	240	0.300	0.080	0.0101	0.0057	0.5741	0.032	28.4	----	------	------
1 1415	255	0.300	0.080	0.0102	0.0057	0.5899	0.061	28.1	----	------	------
1 1430	270	0.297	0.080	0.0105	0.0056	0.6197	0.006	28.0	----	------	------
1 1445	285	0.297	0.083	0.0102	0.0055	0.6225	0.015	27.8	----	------	------
1 1500	300	0.295	0.083	0.0102	0.0054	0.6296	0.048	26.1	----	------	------
1 1515	315	0.295	0.083	0.0104	0.0054	0.6530	0.025	26.1	----	------	------
1 1530	330	0.292	0.083	0.0105	0.0054	0.6650	-0.005	26.1	----	------	------
1 1545	345	0.292	0.080	0.0102	0.0052	0.6625	0.019	25.9	----	------	------
1 1600	360	0.292	----	0.0104	0.0053	0.6718	------	25.8	1.64	0.0010	0.0028

------ NO DATA TAKEN

ITC-380
NOX-AIR IRRADIATON, VARIABLE LIGHT INTEN
1980,NOV 25

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM FN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	PROFALD PPM 10'C-600	ACETONE PPM 10'C-600
1 930	-30	0.0009	0.0011	0.0009	0.0011	0.00220	0.0001	0.0002
1 1145	105	0.0009	-----	0.0009	0.0011	-----	-----	-----
1 1600	360	-----	0.0008	-----	-----	0.00297	0.0003	0.0010

------- NO DATA TAKEN

ITC-381
NOX-AIR IRRADIATION,VAR LIGHT INTENSITY
1980 NOV. 26

0820: FLUSH AND REFILL BAG 3 TIMES.
0912: INJECTIONS MADE DURING FINAL FILL
WITH ~50% R.H. PURE AIR USED.

1015-1315 20% LIGHTS
1315-1530 40% LIGHTS
1600: BAG DUMPED AND REFILLED TWICE.

T=0 AT 1015 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
TS	DORIC-1	26.9	1.3	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.295	PPM
NO2-UNC	T 14B-1	0.088	PPM
PROPANE	DMS-1	0.0094	PPM
PROPENE	DMS-1	0.0092	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2100	PN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID

ITC-381
NOX-AIR IRRADIATION,VAR LIGHT INTENSITY
1980 NOV. 26

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROFANE PPM DMS-1	PROFENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1	ACETYLEN PPM PN-1
1 922	-53	----	----	0.0093	0.0092	----	----	----	----	----	----	----
1 931	-44	----	----	0.0089	0.0087	----	----	----	----	----	----	----
1 934	-41	----	----	----	----	----	----	----	1.66	0.0012	0.0028	0.0014
1 944	-31	----	----	0.0094	0.0092	----	----	----	----	----	----	----
1 954	-21	----	----	0.0093	0.0090	----	----	----	----	----	----	----
1 1015	0	0.295	0.088	0.0094	0.0092	0.0242	0.025	25.6	----	----	----	----
1 1030	15	0.297	0.083	0.0094	0.0090	0.0363	0.001	25.8	----	----	----	----
1 1045	30	0.297	0.085	0.0090	0.0087	0.0366	0.037	25.8	----	----	----	----
1 1100	45	0.295	0.085	0.0088	0.0083	0.0544	0.051	25.6	----	----	----	----
1 1115	60	0.297	0.088	0.0085	0.0078	0.0791	0.010	25.8	----	----	----	----
1 1130	75	0.297	0.088	0.0086	0.0079	0.0839	-0.004	25.8	----	----	----	----
1 1145	90	0.297	0.088	0.0085	0.0078	0.0817	0.042	25.9	----	----	----	----
1 1200	105	0.297	0.088	0.0086	0.0078	0.1021	0.013	25.9	----	----	----	----
1 1215	120	0.297	0.088	0.0086	0.0078	0.1083	0.022	25.9	----	----	----	----
1 1230	135	0.297	0.088	0.0086	0.0076	0.1190	-0.007	25.9	----	----	----	----
1 1245	150	0.297	0.085	0.0086	0.0076	0.1157	0.026	25.9	----	----	----	----
1 1300	165	0.295	0.090	0.0087	0.0076	0.1286	0.020	25.9	----	----	----	----
1 1315	180	0.295	0.088	0.0087	0.0074	0.1385	0.019	25.9	----	----	----	----
1 1330	195	0.295	0.088	0.0086	0.0074	0.1475	0.011	27.6	----	----	----	----
1 1345	210	0.297	0.088	0.0085	0.0073	0.1529	0.049	27.8	----	----	----	----
1 1400	225	0.295	0.088	0.0087	0.0073	0.1769	0.014	28.0	----	----	----	----
1 1415	240	0.295	0.088	0.0082	0.0068	0.1837	0.085	28.7	----	----	----	----
1 1430	255	0.295	0.088	0.0078	0.0063	0.2250	0.001	28.8	----	----	----	----
1 1445	270	0.295	0.088	0.0085	0.0068	0.2253	-0.003	28.7	----	----	----	----
1 1500	285	0.290	0.090	0.0083	0.0067	0.2236	0.054	28.7	----	----	----	----
1 1515	300	0.290	0.088	0.0085	0.0066	0.2498	0.037	28.7	----	----	----	----
1 1530	315	0.290	0.088	0.0085	0.0065	0.2680	----	28.7	1.65	0.0010	0.0025	0.0011

------ NO DATA TAKEN

214

ITC-381
NOX-AIR IRRADIATION,VAR LIGHT INTENSITY
1980 NOV. 26

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600
1 931	-44	0.0007	0.0009	------	------
1 951	-24	------	------	0.00115	0.0003
1 1530	315	0.0007	0.0008	0.00315	0.0003

------ NO DATA TAKEN

215

ITC-382
NOX-AIR IRRADIATION, 3% RH
1980,DEC 2

0900: BAG DUMPED AND FILLED 3 TIMES WITH DRYEST PURE AIR.
0950: PROPANE AND PROPENE INJ., 2.4 ML. NO AND 0.6 ML. NO2 ALSO INJ.
1030: LIGHTS ON - 100%.
1203: DRY PURE AIR CHECK - DRY=293 DEGREES K, WET=280 DEGREES K, R.H.=~3%

T=0 AT 1030 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.035	0.039	PPT
TS	DORIC-1	29.7	1.7	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.334	PPM
NO2-UNC	T 14B-1	0.078	PPM
PROPANE	DMS-1	0.0084	PPM
PROPENE	DMS-1	0.0077	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM PN-1	ETHENE PPM PN-1	ETHANE PPM PN-1
1 1000	-30	------	------	0.0081	0.0074	------	------	------	1.82	0.0020	0.0031
1 1016	-14	------	------	0.0083	0.0076	------	------	------	------	------	------
1 1030	0	0.334	0.078	0.0084	0.0077	0.0984	0.141	24.9	------	------	------
1 1045	15	0.336	0.073	0.0085	0.0072	0.1668	0.042	28.6	------	------	------
1 1100	30	0.336	0.073	0.0085	0.0070	0.1873	0.020	29.3	------	------	------
1 1115	45	0.336	0.073	0.0084	0.0069	0.1970	0.040	29.8	------	------	------
1 1130	60	0.334	0.073	0.0084	0.0067	0.2165	0.004	30.2	------	------	------
1 1145	75	0.336	0.076	0.0083	0.0067	0.2187	0.012	30.3	------	------	------
1 1200	90	0.336	0.073	0.0082	0.0065	0.2243	0.037	30.5	------	------	------
1 1215	105	0.336	0.078	0.0082	0.0064	0.2421	0.023	30.5	------	------	------
1 1230	120	0.334	0.078	0.0083	0.0064	0.2532	0.017	30.7	------	------	------
1 1245	135	0.336	0.073	0.0082	0.0063	0.2613	0.018	30.9	------	------	------
1 1300	150	0.334	0.076	0.0082	0.0062	0.2701	------	30.9	1.81	0.0024	0.0041

------ NO DATA TAKEN

216

ITC-382
NOX-AIR IRRADIATION, 3% RH
1980,DEC 2

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM PN-1	I-C4 FFM DMS-1	N-BUTANE PPM DMS-1	ACETALD PPM 10'C-600	PROFALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1000	-30	0.0032	0.0031	0.0008	0.0009	------	------	------
1 1300	150	0.0031	0.0036	0.0008	0.0009	0.00075	0.0001	0.0002

------ NO DATA TAKEN

ITC-383
NOX - AIR IRRADIATION
1980,DEC 3

FOLLOWS "DUMMY" PROPENE/NOX IRRADIATION ON DEC. 2

0900: DRY PURE AIR FILL WITH ~50% RH, BEGIN BAG FILL AND DUMP 3 TIMES.
0910: SWITCH TO DRY AIR.
1045: LIGHTS ON - 100%.
1249: START N2O INTO BAG.
1312: STOP N2O FLOW INTO BAG.
1608: ALL OFF, DUMP BAG.

T=0 AT 1045 PST

K1 = 0.450 MIN-1

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL	DORIC-1	0.036	0.050	PPT
TS	DORIC-1	29.4	1.9	DEG C

ID	INST.	INITIAL CONC.	UNITS
NO	T 14B-1	0.354	PPM
NO2-UNC	T 14B-1	0.068	PPM
PROPANE	DMS-1	0.0099	PPM
PROPENE	DMS-1	0.0089	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
1510	T 14B-1	TECO 14B-1 NO-NOX NYLON FILTER ANALYZER
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2100	FN-1	RM 121; POROPAK N ; FID
2920	10'C-600	RH-121; 10' 10% CARBOWAX-600; FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM T 14B-1	NO2-UNC PPM T 14B-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT	TS DEG C DORIC-1	METHANE PPM FN-1	ETHENE PPM PN-1	ETHANE PPM PN-1
1 1015	-30	------	------	0.0101	0.0089	------	------	------	2.46	0.0056	0.0102
1 1030	-15	------	------	0.0100	0.0089	------	------	------	------	------	------
1 1045	0	0.354	0.068	0.0099	0.0089	0.1138	0.073	24.6	------	------	------
1 1100	15	0.356	0.066	0.0100	0.0087	0.1493	0.063	29.1	------	------	------
1 1115	30	0.356	0.068	0.0100	0.0084	0.1802	0.020	29.8	------	------	------
1 1130	45	0.356	0.071	0.0099	0.0082	0.1899	-0.029	30.2	------	------	------
1 1145	60	0.356	0.071	0.0098	0.0082	0.1758	-0.118	30.0	------	------	------
1 1200	75	0.354	0.071	0.0101	0.0080	0.2333	-0.004	30.3	------	------	------
1 1215	90	0.354	0.071	0.0076	0.0060	0.2316	-0.059	30.5	------	------	------
1 1230	105	0.354	0.071	0.0094	0.0072	0.2605	-0.012	30.0	------	------	------
1 1245	120	0.354	0.071	0.0099	0.0077	0.2548	------	30.3	------	------	------

------ NO DATA TAKEN

218

ITC-383
NOX - AIR IRRADIATION
1980,DEC 3

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	ACETYLEN PPM DMS-1	ACETYLEN PPM PN-1	I-C4 PPM DMS-1	N-BUTANE PPM DMS-1	BENZENE PPM 10'C-600	ACETALD PPM 10'C-600	ACETONE PPM 10'C-600
1 1015	-30	0.0059	0.0072	0.0007	0.0009	0.0002	0.00360	0.0007

------ NO DATA TAKEN

BAG-401
NOX-AIR IRRADIATION #1
1980,NOV 5

BAG #4 FILLED WITH SCOTT MARRIN ULTRA-ZERO AIR
1450; NO, NO2, PROPANE, PROPENE INJECTED

T=0 AT 1529 PST

K1 = 0.270 MIN-1

BAG NO. 4 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.202	0.112	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	COL-1600	0.460	PPM
NO2-UNC	COL-1600	0.155	PPM
PROPANE	DMS-2	0.0209	PPM
PROPENE	DMS-2	0.0219	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID
1625	COL-1600	COLUMBIA NOX ANALYZER, MODEL 1600

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM COL-1600	NO2-UNC PPM COL-1600	PROPANE PPM DMS-2	PROPENE PPM DMS-2	LNC3/C3=	HYDROXYL PPT
1 1512	-17	0.460	0.155	------	------	------	------
1 1529	0	------	------	0.0209	0.0219	-0.0492	0.164
1 1544	15	0.455	0.153	0.0204	0.0198	0.0307	0.079
1 1559	30	0.436	0.155	0.0206	0.0192	0.0693	0.122
1 1614	45	0.407	0.165	0.0208	0.0181	0.1287	0.071
1 1629	60	0.377	0.175	0.0208	0.0176	0.1635	0.201
1 1646	77	0.340	0.199	0.0199	0.0151	0.2747	0.267
1 1659	90	0.300	0.221	0.0206	0.0140	0.3873	0.124
1 1714	105	0.262	0.242	0.0200	0.0128	0.4479	0.261
1 1729	120	0.214	0.273	0.0201	0.0113	0.5751	0.221
1 1744	135	0.162	0.298	0.0204	0.0103	0.6829	0.150
1 1759	150	0.119	0.316	------	------	------	------
1 1806	157	------	------	0.0204	0.0093	0.7897	0.472
1 1814	165	0.081	0.326	0.0203	0.0081	0.9124	0.294
1 1829	180	0.060	0.326	0.0204	0.0071	1.055	------

------ NO DATA TAKEN

220

BAG-402
NOX-AIR IRRADIATION #2
1980, NOV 6

BAG #4 FILLED WITH ULTRA-ZERO AIR (SCOTT-MARRIN)
1123: NO, NO2, PROPANE, PROPENE INJECTED

T=0 AT 1150 PST

K1 = 0.270 MIN-1

BAG NO.   4 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.145	0.057	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	COL-1600	0.475	PPM
NO2-UNC	COL-1600	0.220	PPM
PROPANE	DMS-2	0.0228	PPM
PROPENE	DMS-2	0.0228	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID
1625	COL-1600	COLUMBIA NOX ANALYZER, MODEL 1600

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM COL-1600	NO2-UNC PPM COL-1600	PROPANE PPM DMS-2	PROPENE PPM DMS-2	LNC3/C3= RAW DATA	HYDROXYL PPT
1 1150	0	0.475	0.220	0.0228	0.0228	-0.0018	0.062
1 1205	15	0.477	0.220	0.0220	0.0214	0.0285	0.138
1 1220	30	0.467	0.210	0.0227	0.0206	0.0957	0.124
1 1235	45	0.455	0.210	0.0221	0.0189	0.1558	0.140
1 1250	60	0.441	0.209	0.0219	0.0175	0.2238	0.097
1 1305	75	0.421	0.216	0.0213	0.0162	0.2711	0.180
1 1320	90	0.401	0.216	0.0218	0.0163	0.3585	0.175
1 1335	105	0.375	0.224	0.0222	0.0143	0.4437	0.248
1 1350	120	0.355	0.229	0.0217	0.0124	0.5647	-----

----- NO DATA TAKEN

BAG-403
NOX-AIR IRRADIATION #3
1980,NOV 7

BAG #4 FILLED WITH ULTRA-ZERO AIR (SCOTT-MARRIN)
1057: NO, NO2, PROPANE, PROPENE INJECTED

T=0 AT 1120 PST

K1 = 0.270 MIN-1

BAG NO.   4 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.121	0.061	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	COL-1600	0.476	PPM
NO2-UNC	COL-1600	0.135	PPM
PROPANE	DMS-2	0.0210	PPM
PROPENE	DMS-2	0.0166	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID
1625	COL-1600	COLUMBIA NOX ANALYZER, MODEL 1600

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM COL-1600	NO2-UNC PPM COL-1600	PROPANE PPM DMS-2	PROPENE PPM DMS-2	LNC3/C3= RAW DATA	HYDROXYL PPT
1 1120	0	0.476	0.135	0.0210	0.0166	0.2337	0.066
1 1135	15	0.470	0.135	0.0207	0.0159	0.2657	0.082
1 1150	30	0.462	0.135	0.0202	0.0149	0.3056	0.144
1 1205	45	0.455	0.140	0.0223	0.0153	0.3757	0.067
1 1220	60	0.439	0.139	0.0199	0.0132	0.4082	0.184
1 1235	75	0.424	0.146	0.0210	0.0128	0.4977	0.112
1 1250	90	0.401	0.156	0.0193	0.0111	0.5525	0.233
1 1305	105	0.379	0.166	0.0218	0.0112	0.6660	0.083
1 1320	120	0.359	0.170	0.0203	0.0100	0.7066	-----

------ NO DATA TAKEN

222

BAG-404
C3/C3= NOX PHOTOLYSIS #4
1980,NOV 10

BAG #4 FILLED WITH ULTRA-ZERO AIR (SCOTT-MARRIN)
1025: NO, NO2, PROPANE, PROPENE INJECTED

T=0 AT 1202 PST

K1 = 0.270 MIN-1

BAG NO. 4 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.164	0.047	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	DMS-2	0.503	PPM
NO2-UNC	DMS-2	0.120	PPM
PROPANE	DMS-2	0.0134	PPM
PROPENE	DMS-2	0.0144	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM DMS-2	NO2-UNC PPM DMS-2	PROPANE PPM DMS-2	PROPENE PPM DMS-2	LNC3/C3= RAW DATA	HYDROXYL PPT
1 1202	0	0.503	0.120	0.0134	0.0144	-0.0670	0.092
1 1218	16	0.499	0.128	0.0139	0.0142	-0.0192	0.103
1 1231	29	0.484	0.132	0.0134	0.0131	0.0242	0.165
1 1247	45	0.470	0.138	0.0139	0.0125	0.1100	0.145
1 1302	60	0.451	0.145	0.0137	0.0115	0.1804	0.211
1 1317	75	0.423	0.156	0.0141	0.0106	0.2830	0.177
1 1332	90	0.399	0.165	0.0132	0.0091	0.3693	0.216
1 1347	105	0.363	0.180	0.0134	0.0084	0.4743	0.200
1 1402	120	0.333	0.191	0.0132	0.0074	0.5718	-----

----- NO DATA TAKEN

BAG-405
NOX-AIR IRRADIATION #5
1980,NOV 12

BAG #4 FILLED WITH ULTRA-ZERO AIR (SCOTT-MARRIN)
0933: NO, NO2, PROPANE, PROPENE INJECTED

T=0 AT 1124 PST

K1 = 0.270 MIN-1

BAG NO. 4 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.188	0.063	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	COL-1600	0.467	PPM
NO2-UNC	COL-1600	0.119	PPM
PROPANE	DMS-2	0.0127	PPM
PROPENE	DMS-2	0.0141	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2290	DMS-2	RM-103; DIMETHYLSULFOLANE W/FID
1625	COL-1600	COLUMBIA NOX ANALYZER, MODEL 1600

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO FPM COL-1600	NO2-UNC FPM COL-1600	PROPANE FPM DMS-2	PROPENE FPM DMS-2	LNC3/C3= RAW DATA	HYDROXYL FPT
1 1124	0	0.467	0.119	0.0127	0.0141	-0.1024	0.209
1 1139	15	0.461	0.121	0.0132	0.0132	-0.0008	0.127
1 1154	30	0.440	0.129	0.0128	0.0121	0.0610	0.237
1 1209	45	0.423	0.135	0.0132	0.0111	0.1764	0.133
1 1224	60	0.403	0.147	0.0131	0.0103	0.2414	0.195
1 1239	75	0.377	0.155	0.0124	0.0089	0.3363	0.294
1 1254	90	0.351	0.170	0.0130	0.0081	0.4794	0.106
1 1309	105	0.328	0.180	0.0124	0.0073	0.5309	0.207
1 1324	120	0.301	0.189	0.0132	0.0070	0.6315	------

------ NO DATA TAKEN

OK,

BAG-501
C3/C3= NOX PHOTOLYSIS #1
1981, FEB 3

BAG #5 FILLED WITH SCOTT-MARRIN ULTRA-ZERO AIR
  1100: NO, NO2, PROPANE, PROPENE INJECTED
ALL INJECTIONS MADE WITH SYRINGE PUMPED 10 TIMES.
NO: 2.9 ML NO IN 97.1 ML N2. 1 ML OF THIS MIXED WITH 99 ML N2
AND INJECTED INTO BAG.
NO2: 0.7 ML NO IN 99.3 ML O2. 1 ML OF THIS IN 99 ML O2 INJECTED
INTO THE BAG
PROPANE: 0.7 ML C3 IN 99.3 ML N2. 1 ML OF THIS MIXED WITH 99 ML
N2 AND INJECTED INTO THE BAG.
PROPENE: 0.7 ML PROPENE IN 99.3 ML N2. 1 ML OF THIS MIXED INTO
99 ML N2. 10 ML OF THIS MIXED INTO 90 ML N2.

T=0 AT 1410 PST

BAG NO.   5 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.056	0.019	PPT

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.345	PPM
NO2-UNC	B-NOX-1	0.227	PPM
PROPANE	DMS-1	0.0091	PPM
PROPENE	DMS-1	0.0074	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN30003B-2

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL PPT
1 1351	-19	0.351	0.226	0.0094	0.0075	0.2277	-----
1 1410	0	0.345	0.227	0.0091	0.0074	0.2091	0.073
1 1425	15	0.358	0.206	0.0092	0.0072	0.2447	0.075
1 1440	30	0.361	0.191	0.0092	0.0069	0.2811	0.029
1 1455	45	0.366	0.186	0.0092	0.0068	0.2954	0.055
1 1510	60	0.364	0.177	0.0091	0.0066	0.3221	0.035
1 1525	75	0.363	0.174	0.0089	0.0064	0.3392	0.082
1 1540	90	0.359	0.169	0.0087	0.0060	0.3792	0.053
1 1555	105	0.356	0.166	0.0084	0.0056	0.4051	0.047
1 1616	126	0.348	0.165	0.0088	0.0057	0.4370	-----

------ NO DATA TAKEN

BAG-502
NOX-C3/C3= IRRADIATION #2
1981, MAR 5

BAG #5 FILLED WITH SCOTT-MARRIN ULTRA ZERO AIR UNDER RED LIGHTS.
NO, NO2, PROPANE, PROFENE INJECTED
NO: 2.9 ML NO IN 97.1 ML N2, 1 ML OF THIS MIXED WITH 99 ML N2
AND INJECTED INTO BAG.
NO2: 0.7 ML NO IN 99.3 ML O2, 1 ML OF THIS MIXED WITH 99 ML O2
AND INJECTED INTO THE BAG.
PROPANE: 0.7 ML C3 IN 99.3 ML N2, 1 ML OF THIS MIXED WITH 99 ML
N2 AND INJECTED INTO THE BAG.
PROPENE: 0.7 ML C3= IN 99.3 ML N2, 1 ML OF THIS MIXED WITH 99 ML
N2, AND 10 ML OF THIS MIXED WITH 90 ML N2 AND INJECTED INTO BAG.

T=0 AT 1126 FST

BAG NO.   5 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS
HYDROXYL		0.048	0.049	FFT

ID	INST.	INITIAL CONC.	UNITS
NO	B-NOX-1	0.269	PPM
NO2-UNC	B-NOX-1	0.100	PPM
PROPANE	DMS-1	0.0095	PPM
PROFENE	DMS-1	0.0083	PPM

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
4600	B-NOX-1	BENDIX NOX ANALYZER M08101BX SN300038-2

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	NO PPM B-NOX-1	NO2-UNC PPM B-NOX-1	PROPANE PPM DMS-1	PROPENE PPM DMS-1	LNC3/C3=	HYDROXYL FFT
1 1103	-23	0.264	0.100	0.0103	0.0091	0.1195	-----
1 1126	0	0.269	0.100	0.0095	0.0083	0.1377	0.042
1 1141	15	0.249	0.091	0.0099	0.0085	0.1581	0.120
1 1156	30	0.256	0.099	0.0098	0.0079	0.2164	-0.024
1 1211	45	0.250	0.094	0.0095	0.0077	0.2049	0.105
1 1226	60	0.245	0.098	0.0100	0.0077	0.2559	0.071
1 1241	75	0.242	0.093	0.0095	0.0071	0.2907	0.047
1 1256	90	0.246	0.090	0.0091	0.0067	0.3138	0.012
1 1311	105	0.236	0.095	0.0095	0.0069	0.3195	0.009
1 1326	120	0.232	0.091	0.0094	0.0068	0.3239	-----

------- NO DATA TAKEN

ARB- 1
NOX - AIR IRRADIATION: EFFECTS OF NH3
1980,OCT 21

OCT 21
919: RH   DRY:28   WET:10.6   RH<10%
1005: INJECT 5 ML NO2
1007: INJECT 15 ML NO
1009: INJECT .32 ML C3 AND .32 ML C3=
1135: DIVIDE BAG
1139-1141: INJECT 20 ML NH3 INTO SIDE A
1200: UNCOVER BAG (T=0)
1420: BAG COVERED

T=0 AT 1200 PST

BAG NO.   18 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS	
HYDROXYL		0.043	0.034	PPT	SIDE 1
HYDROXYL		0.040	0.007	PPT	SIDE 2
TS	DORIC-1	31.8	2.1	DEG C	SIDE 1
TS	DORIC-1	31.4	1.9	DEG C	SIDE 2
K1		0.348	0.067	MIN-1	SIDE 1
K1		0.335	0.070	MIN-1	SIDE 2

ID	INST.	INITIAL CONC.	UNITS	
NO	B-NOX-1	0.366	PPM	SIDE 1
NO	B-NOX-1	0.369	PPM	SIDE 2
NO2-UNC	B-NOX-1	0.150	PPM	SIDE 1
NO2-UNC	B-NOX-1	0.151	PPM	SIDE 2
PROPANE	DMS-1	0.0102	PPM	SIDE 1
PROPANE	DMS-1	0.0108	PPM	SIDE 2
PROPENE	DMS-1	0.0084	PPM	SIDE 1
PROPENE	DMS-1	0.0090	PPM	SIDE 2

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID
2100	FN-1	RM-121; POROPAK N ; FID
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MD8101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN100015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2000	ECD-1	RM-121; 12' 5% CARBOWAX-400; ECD
4130	EPPLEY	ARB LAB; EPPLEY 11692 UV RADIOMETER
4300	TSI 023	TSI ELECTRICAL AEROSOL ANALYZER MD:3030
4350	CLIMET	CLIMET OPC MD:208 SN76-148
4400	MRI 388	MRI INTEGRATING NEPHELOMETER MD:1550B
4200	CNC-143	ENV. ONE CNC MD:RICH100, SN:143

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ARB- 1
NOX - AIR IRRADIATION: EFFECTS OF NH3
1980,OCT 21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 OZONE PPM D-1790	SIDE 2 OZONE PPM D-1790	SIDE 1 NO PPM B-NOX-1	SIDE 2 NO PPM B-NOX-1	SIDE 1 NO2-UNC PPM B-NOX-1	SIDE 2 NO2-UNC PPM B-NOX-1	SIDE 1 NOX-UNC PPM B-NOX-1	SIDE 2 NOX-UNC PPM B-NOX-1	SIDE 1 PROPANE PPM DMS-1	SIDE 2 PROPANE PPM DMS-1
1 950	-130	0.001	0.001	0.001	0.001	0.005	0.005	0.009	0.009	----	----
1 1116	-44	----	0.001	----	0.369	----	0.151	----	0.522	0.0108	0.0108
1 1120	-40	0.001	----	0.368	----	0.149	----	0.516	----	----	----
1 1150	-10	0.002	0.004	0.366	0.352	0.150	0.143	0.516	0.495	0.0102	0.0104
1 1200	0	----	----	----	----	----	----	----	----	0.0085	0.0085
1 1215	15	0.004	----	0.360	----	0.149	----	0.504	----	0.0104	0.0086
1 1230	30	----	0.003	----	0.352	----	0.143	----	0.496	----	----
1 1245	45	0.005	----	0.360	----	0.145	----	0.502	----	----	----
1 1300	60	----	0.002	----	0.351	----	0.141	----	0.494	----	----
1 1315	75	0.005	----	0.354	----	0.138	----	0.490	----	0.0122 R	0.0105
1 1330	90	0.005	0.003	----	0.350	----	0.140	----	0.488	----	----
1 1345	105	----	----	0.354	----	0.140	----	0.494	----	0.0104	0.0095
1 1400	120	0.004	----	----	----	----	----	----	----	----	----
1 1415	135	----	0.003	----	0.343	----	0.138	----	0.480	----	----
1 1421	141	----	----	----	----	----	----	----	----	----	----

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PROPENE PPM DMS-1	SIDE 2 PROPENE PPM DMS-1	SIDE 1 LNC3/C3=	SIDE 2 LNC3/C3=	SIDE 1 HYDROXYL PPT	SIDE 2 HYDROXYL PPT	SIDE 1 TS DEG C DORIC-1	SIDE 2 TS DEG C DORIC-1	SIDE 1 K1 MIN-1	SIDE 2 K1 MIN-1
1 950	-130	----	----	----	----	----	----	27.3	27.3	----	----
1 1116	-44	0.0090	0.0090	0.1886	0.1886	----	----	----	30.9	----	----
1 1120	-40	----	----	----	----	----	----	----	----	----	----
1 1150	-10	0.0084	0.0084	0.1903	----	----	----	32.0	----	----	----
1 1200	0	----	----	----	0.2149	0.009	0.032	31.1	32.3	0.448 A	0.440 A
1 1215	15	0.0070	0.0067	0.1995	----	0.078	----	32.2	32.3	0.353	0.351
1 1230	30	----	----	----	0.2461	----	0.045	----	----	0.360	0.325
1 1245	45	0.0079	0.0075	0.2758	----	----	----	33.0	31.5	----	----
1 1300	60	----	----	----	----	----	----	----	----	----	----
1 1315	75	0.0070	----	----	----	----	----	33.5	32.6	0.312	0.312
1 1330	90	----	----	----	0.3339	0.042	0.042	----	----	----	----
1 1345	105	0.0073	----	0.3580	----	----	----	33.3	32.6	0.267	0.246
1 1400	120	----	0.0065	----	0.3832	----	----	----	----	----	----
1 1415	135	----	----	----	----	----	----	----	----	----	----
1 1421	141	----	----	----	----	----	----	----	----	----	----

------ NO DATA TAKEN

ARB- 1
NOX - AIR IRRADIATION: EFFECTS OF NH3
1980,OCT 21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 UV RAD MW/CM2 EPPLEY	SIDE 2 UV RAD MW/CM2 EPPLEY	SIDE 1 PAN PPM ECD-1	SIDE 2 PAN PPM ECD-1	SIDE 1 CO PPM BK6800-1	SIDE 2 CO PPM BK6800-1	SIDE 1 THC FPMC BK6800-1	SIDE 2 THC FPMC BK6800-1
1 950	-130	----	----	----	----	1.38	1.38	1.19	1.19
1 1120	-40	----	----	----	0.000	----	1.45	----	1.32
1 1150	-10	----	----	0.000	----	1.33	----	1.34	----
1 1200	0	3.28	3.21	----	----	1.43	1.42	1.30	1.34
1 1215	15	----	----	----	----	1.46	1.34	1.28	1.30
1 1230	30	2.56	2.52	----	----	----	----	----	----
1 1245	45	----	----	----	----	----	----	----	----
1 1300	60	2.55	2.26	----	----	1.50	1.41	1.47	1.27
1 1315	75	----	----	----	----	----	----	----	----
1 1330	90	2.13	2.08	----	----	1.46	1.45	1.40	1.33
1 1345	105	----	----	----	----	----	----	----	----
1 1400	120	1.73	1.55	----	----	1.40	1.49	1.30	1.35
1 1415	135	----	----	----	----	----	----	----	----

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 METHANE PPM FN-1	SIDE 2 METHANE PPM BK6800-1	SIDE 1 METHANE PPM BK6800-1	SIDE 2 METHANE PPM FN-1	SIDE 1 ETHENE PPM PN-1	SIDE 2 ETHENE PPM PN-1	SIDE 1 ETHANE PPM PN-1	SIDE 2 ETHANE PPM PN-1	SIDE 1 ACETYLEN PPM PN-1	SIDE 2 ACETYLEN PPM PN-1
1 950	-130	----	1.68	1.68	----	----	----	----	----	----	----
1 1116	-44	1.75	----	----	1.75	0.0023	0.0023	0.0024	0.0024	0.0023	0.0023
1 1120	-40	----	1.73	----	----	----	----	----	----	----	----
1 1150	-10	----	----	1.66	----	----	----	----	----	----	----
1 1200	0	----	1.68	1.66	----	----	----	----	----	----	----
1 1215	15	----	----	1.68	----	----	----	----	----	----	----
1 1230	30	----	1.63	----	----	----	----	----	----	----	----
1 1245	45	----	----	----	----	----	----	----	----	----	----
1 1300	60	----	1.64	1.67	----	----	----	----	----	----	----
1 1315	75	----	----	----	----	----	----	----	----	----	----
1 1330	90	----	1.66	1.66	----	----	----	----	----	----	----
1 1345	105	----	----	----	----	----	----	----	----	----	----
1 1400	120	1.78	1.67	1.65	1.78	0.0011	0.0020	0.0024	0.0023	0.0020	0.0023
1 1415	135	----	----	----	----	----	----	----	----	----	----

------ NO DATA TAKEN

ARB- 1
NOX - AIR IRRADIATION: EFFECTS OF NH3
1980,OCT 21

CLOCK TIME HR. DY	ELAPSED TIME (MIN)	SIDE 1 BENZENE PPM 10'C-600	SIDE 2 BENZENE PPM 10'C-600	SIDE 1 ACETALD PPM 10'C-600	SIDE 2 ACETALD PPM 10'C-600	SIDE 1 CONDENS CNT*10E3 CNC-143	SIDE 2 CONDENS CNT*10E3 CNC-143	SIDE 1 #PART>.3 PART/CC CLIMET	SIDE 2 #PART>.3 PART/CC CLIMET	SIDE 1 #PART>.5 PART/CC CLIMET	SIDE 2 #PART>.5 PART/CC CLIMET
1 950	-130	---	---	---	---	0.7	0.7	6.	6.	1.	1.
1 1116	-44	0.0002	0.0002	0.003	0.003	---	0.4	---	3.	---	1.
1 1120	-40	---	---	---	---	3.0	---	2.	---	1.	---
1 1150	-10	---	---	---	---	2.9	---	3.	---	0.	---
1 1200	0	---	---	---	---	---	0.2	---	2.	---	0.
1 1215	15	---	---	---	---	3.0	---	13.	---	0.	---
1 1230	30	---	---	---	---	---	0.4	---	4.	---	0.
1 1245	45	---	---	---	---	2.7	---	70.	---	0.	---
1 1300	60	---	---	---	---	---	0.2	---	6.	---	1.
1 1315	75	---	---	---	---	2.6	---	121.	---	3.	---
1 1330	90	---	---	---	0.004	---	0.2	---	3.	---	0.
1 1345	105	---	---	---	---	---	---	126.	---	4.	---
1 1400	120	0.0002	0.0002	0.005	---	2.7	0.4	---	7.	---	2.
1 1415	135	---	---	---	---	---	---	---	---	---	---

CLOCK TIME HR. DY	ELAPSED TIME (MIN)	SIDE 1 #PART>1 PART/CC CLIMET	SIDE 2 #PART>1 PART/CC CLIMET	SIDE 1 BSCAT 10-4 M-1 MRI 388	SIDE 2 BSCAT 10-4 M-1 MRI 388	SIDE 1 AER.V UM3/CC TSI 023	SIDE 2 AER.V UM3/CC TSI 023	SIDE 1 AER.N PART/CC TSI 023	SIDE 2 AER.N PART/CC TSI 023	SIDE 1 AER.S UM2/CC TSI 023	SIDE 2 AER.S UM2/CC TSI 023
1 950	-130	0.	0.	0.2	0.2	1.	1.	810.	810.	21.	21.
1 1120	-40	0.	0.	0.2	0.2	10.	0.	6132.	662.	310.	6.
1 1150	-10	0.	---	0.2	---	8.	---	5132.	---	266.	---
1 1200	0	0.	---	---	---	---	---	---	---	---	---
1 1215	15	---	---	0.3	0.2	10.	1.	5430.	382.	309.	11.
1 1230	30	0.	0.	---	---	---	---	---	---	---	15.
1 1245	45	---	---	0.3	0.2	8.	1.	5548.	388.	281.	---
1 1300	60	0.	0.	---	---	---	---	---	---	---	9.
1 1315	75	---	---	0.3	0.2	8.	1.	5172.	356.	246.	---
1 1330	90	1.	---	---	---	---	---	---	---	---	6.
1 1345	105	---	---	0.3	0.2	6.	0.	4992.	439.	205.	---
1 1400	120	0.	---	---	---	---	0.	---	417.	---	7.
1 1415	135	---	1.	---	0.2	---	---	---	---	---	---

------- NO DATA TAKEN

ARB- 1
NOX - AIR IRRADIATION; EFFECTS OF NH3
1980,OCT 21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PART.024 PART/CC TSI 023	SIDE 2 PART.024 PART/CC TSI 023	SIDE 1 PART.042 PART/CC TSI 023	SIDE 2 PART.042 PART/CC TSI 023	SIDE 1 PART.075 PART/CC TSI 023	SIDE 2 PART.075 PART/CC TSI 023	SIDE 1 PART.133 PART/CC TSI 023	SIDE 2 PART.133 PART/CC TSI 023	SIDE 1 PART.237 PART/CC TSI 023	SIDE 2 PART.237 PART/CC TSI 023
1 950	-130	334.	334.	174.	174.	178.	178.	96.	96.	25.	25.
1 1120	-40	-----	501.	-----	0.	-----	89.	-----	72.	418.	0.
1 1150	-10	334.	-----	696.	-----	1421.	-----	3229.	-----	381.	-----
1 1200	0	167.	167.	174.	0.	1687.	133.	2699.	72.	455.	12.
1 1215	15	-----	-----	-----	-----	-----	-----	-----	-----	-----	12.
1 1230	30	334.	167.	174.	0.	1332.	133.	3085.	72.	430.	12.
1 1245	45	167.	-----	-----	87.	-----	44.	-----	-----	344.	12.
1 1300	60	-----	167.	522.	-----	1510.	-----	2892.	48.	234.	-----
1 1315	75	334.	-----	-----	0.	-----	44.	-----	-----	-----	-----
1 1330	90	-----	334.	435.	-----	1643.	-----	2386.	48.	-----	-----
1 1345	105	501.	-----	-----	0.	-----	-----	-----	-----	-----	-----
1 1400	120	-----	167.	348.	-----	1909.	178.	1976.	72.	-----	0.
1 1415	135	-----	-----	-----	0.	-----	-----	-----	-----	-----	-----

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PART.422 PART/CC TSI 023	SIDE 2 PART.422 PART/CC TSI 023	SIDE 1 PART.750 PART/CC TSI 023	SIDE 2 PART.750 PART/CC TSI 023
1 950	-130	0.	0.	4.	4.
1 1120	-40	-----	0.	-----	0.
1 1150	-10	27.	-----	7.	-----
1 1200	0	20.	-7.	4.	4.
1 1215	15	-----	-----	-----	-----
1 1230	30	47.	0.	4.	4.
1 1245	45	27.	-7.	0.	4.
1 1300	60	-----	-----	-----	-----
1 1315	75	27.	0.	4.	4.
1 1330	90	-----	-----	-----	-----
1 1345	105	20.	0.	4.	0.
1 1400	120	-----	-----	-----	-----
1 1415	135	-----	0.	-----	0.

----- NO DATA TAKEN

NOTES

R   REJECTED
A   K1 CALCULATED FROM UV RADIOMETER DATA

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ARB- 2
NOX-HNO3 AIR IRRADIATION: EFFECT OF NH3
1980, OCT 22

OCT 22
1005-1020: INJECT .5 ML HNO3/H2O (1:10)
1106: NOX BACKGROUND
    WITHOUT NYLON FILTER   NO:.000 NO2:.003 NOX:.008
    WITH NYLON FILTER   NO:.002 NO2:.011 NOX:.018
    WITHOUT NYLON FILTER   NO:.001 NO2:.006 NOX:.011
1133: INJECT 5 ML NO2
1135: INJECT 15 ML NO
1137: INJECT .32 ML C3 AND .32 ML C3=
1150: DIVIDE BAG
1154-1156: INJECT 20 ML NH3 INTO SIDE A
1230: UNCOVER BAG (T=0)

T=0 AT 1230 PST

BAG NO.   18 USED

ID	INST.	AVERAGE VALUE	S.DEV	UNITS	
HYDROXYL		0.035	0.029	PPM	SIDE 1
HYDROXYL		0.036	0.036	PPM	SIDE 2
TS	DORIC-1	30.6	0.7	DEG C	SIDE 1
TS	DORIC-1	30.3	0.7	DEG C	SIDE 2
K1		0.251	0.057	MIN-1	SIDE 1
K1		0.253	0.061	MIN-1	SIDE 2

ID	INST.	INITIAL CONC.	UNITS	
NO	B-NOX-1	0.401	PPM	SIDE 1
NO	B-NOX-1	0.397	PPM	SIDE 2
NO2-UNC	B-NOX-1	0.137	PPM	SIDE 1
NO2-UNC	B-NOX-1	0.137	PPM	SIDE 2
PROPANE	DMS-1	0.0107	PPM	SIDE 1
PROPANE	DMS-1	0.0093	PPM	SIDE 2
PROPENE	DMS-1	0.0093	PPM	SIDE 1
PROPENE	DMS-1	0.0090	PPM	SIDE 2

INSTRUMENTS USED

ID	LABEL	DESCRIPTION
1790	D-1790	DASIBI 1790 OZONE MONITOR
4600	B-NOX-1	BENDIX NOX ANALYZER MD:101BX SN300038-2
4850	BK6800-1	BECKMAN HYDROCARBON GC MD 6800 SN1000015D
1800	DORIC-1	DORIC TEMP INDICATOR, SN 61479
2000	ECD-1	RM-121; 12* 5% CARBOWAX-400; ECD
4130	EPPLEY	ARB LAB; EFPLEY 11692 UV RADIOMETER
4300	TSI 023	TSI ELECTRICAL AEROSOL ANALYZER MD:3030
4350	CLIMET	CLIMET OPC MD:208 SN76-148
4400	MRI 388	MRI INTEGRATING NEPHELOMETER MD:1550B
4200	CNC-143	ENV. ONE CNC MD:RICH100, SN:143
2920	10'C-600	RM-121; 10' 10% CARBOWAX-600; FID
2100	PN-1	RM 121; POROPAK N ; FID
2200	DMS-1	RM-121; DIMETHYLSULFOLANE; FID

ARB- 2
NOX-HNO3 AIR IRRADIATION; EFFECT OF NH3
1980, OCT 22

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 OZONE PPM D-1790	SIDE 2 OZONE PPM D-1790	SIDE 1 NO PPM B-NOX-1	SIDE 2 NO PPM B-NOX-1	SIDE 1 NO2-UNC PPM B-NOX-1	SIDE 2 NO2-UNC PPM B-NOX-1	SIDE 1 NOX-UNC PPM B-NOX-1	SIDE 2 NOX-UNC PPM B-NOX-1	SIDE 1 PROFANE PPM DMS-1	SIDE 2 PROFANE PPM DMS-1
1 1205	-25	------	------	------	------	------	------	------	------	------	0.0093
1 1215	-15	------	0.002	0.401	0.397	0.137	0.137	0.534	0.532	------	------
1 1225	-5	0.003	------	------	------	------	------	------	------	0.0107	0.0101
1 1230	0	------	0.003	0.399	0.393	0.136	0.138	0.534	0.530	0.0099	0.0094
1 1245	15	------	------	------	------	------	------	------	------	------	------
1 1300	30	0.002	0.003	0.396	0.388	0.138	0.133	0.526	0.520	0.0100	0.0093
1 1315	45	------	------	------	------	------	------	------	------	------	------
1 1330	60	0.002	0.004	0.389	0.382	0.124	0.132	0.522	0.514	0.0103	0.0104
1 1345	75	------	------	------	------	------	------	------	------	------	------
1 1400	90	0.003	0.004	0.388	0.378	0.130	0.132	0.517	0.512	0.0107	0.0108
1 1415	105	------	------	------	------	------	------	------	------	------	------
1 1430	120	0.004	0.004	------	0.382	------	0.132	------	0.516	------	------
1 1445	135	------	------	------	------	------	------	------	------	------	------

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PROFENE PPM DMS-1	SIDE 2 PROFENE PPM DMS-1	SIDE 1 LNC3/C3=	SIDE 2 LNC3/C3=	SIDE 1 HYDROXYL PPM	SIDE 2 HYDROXYL PPM	SIDE 1 TS DEG C DORIC-1	SIDE 2 TS DEG C DORIC-1	SIDE 1 K1 MIN-1	SIDE 2 K1 MIN-1
1 1205	-25	------	0.0086	------	0.0728	------	0.078	------	------	------	------
1 1215	-15	------	------	------	------	------	------	30.0	30.0	------	------
1 1225	-5	0.0093	------	------	------	0.015	-0.016	------	------	------	------
1 1230	0	------	0.0085	0.1322	0.1746	------	------	30.9	29.3	0.320 A	0.336 A
1 1245	15	0.0086	------	------	------	0.065	0.035	------	------	------	------
1 1300	30	------	0.0080	0.1472	0.1595	------	------	31.2	30.7	0.272	0.286
1 1315	45	0.0081	------	------	------	0.055	0.061	------	------	------	------
1 1330	60	------	0.0077	0.2103	0.1933	------	------	31.2	31.0	0.215	0.244
1 1345	75	0.0079	------	------	------	0.006	0.022	------	------	------	------
1 1400	90	------	0.0081	0.2640	0.2522	------	------	29.8	30.8	0.195	0.226
1 1415	105	0.0082	------	------	------	------	------	------	------	------	------
1 1430	120	------	0.0082	0.2700	0.2741	------	------	------	29.9	------	0.175
1 1445	135	------	------	------	------	------	------	------	------	------	------

------ NO DATA TAKEN

ARB- 2

NOX-HNO3 AIR IRRADIATION: EFFECT OF NH3

1980, OCT 22

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 UV RAD MW/CM2 EPPLEY	SIDE 2 UV RAD MW/CM2 EPPLEY	SIDE 1 FAN PPM ECD-1	SIDE 2 FAN PPM ECD-1	SIDE 1 CO PPM BK6800-1	SIDE 2 CO PPM BK6800-1	SIDE 1 THC FFMC BK6800-1	SIDE 2 THC FFMC BK6800-1
1 1215	-15	------	------	------	0.000	------	1.23	------	1.47
1 1225	-5	------	------	0.000	------	1.18	------	1.30	------
1 1245	15	------	2.40	------	------	------	1.32	------	1.37
1 1300	30	2.26	1.98	------	------	1.39	------	1.39	------
1 1315	45	1.85	1.62	------	------	------	1.36	------	1.45
1 1330	60	------	------	------	------	1.26	------	1.32	------
1 1345	75	1.39	1.42	------	------	------	1.37	------	1.33
1 1400	90	------	------	------	------	1.37	------	1.22	------
1 1415	105	1.19	1.03	0.000	------	------	1.36	------	1.27
1 1430	120	------	------	------	------	1.34	------	1.21	------
1 1445	135	------	------	0.000	0.000	------	1.35	------	1.21

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 METHANE PPM BK6800-1	SIDE 2 METHANE PPM PN-1	SIDE 1 ETHENE PPM PN-1	SIDE 2 ETHENE PPM PN-1	SIDE 1 ETHANE PPM PN-1	SIDE 2 ETHANE PPM PN-1	SIDE 1 ACETYLEN PPM PN-1	SIDE 2 ACETYLEN PPM PN-1
1 1205	-25	------	1.92	------	0.0023	------	0.0035	------	0.0024
1 1215	-15	------	------	------	------	------	------	------	------
1 1225	-5	1.82	------	------	------	------	------	------	------
1 1230	0	------	1.92	------	------	------	------	------	------
1 1245	15	1.82	------	------	------	------	------	------	------
1 1300	30	------	1.92	------	------	------	------	0.0024	------
1 1315	45	1.84	------	0.0024	------	0.0037	------	------	------
1 1330	60	------	1.87	------	------	------	------	------	------
1 1345	75	1.82	------	------	------	------	------	------	------
1 1400	90	------	1.85	------	------	------	------	------	------
1 1415	105	1.81	------	------	------	------	------	0.0025	------
1 1430	120	------	1.81	0.0021	------	0.0039	------	------	------
1 1445	135	------	1.94	------	0.0022	------	0.0040	------	0.0026

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 C3=/C3 PPM	SIDE 2 C3=/C3 PPM	SIDE 1 BENZENE PPM 10'C-600	SIDE 2 BENZENE PPM 10'C-600	SIDE 1 ACETALD PPM 10'C-600	SIDE 2 ACETALD PPM 10'C-600	SIDE 1 CONDENS CNT*10E3 CNC-143	SIDE 2 CONDENS CNT*10E3 CNC-143	SIDE 1 #PART>.3 PART/CC CLIMET	SIDE 2 #PART>.3 PART/CC CLIMET
1 1205	-25	------	0.8020	------	0.0001	------	0.002	------	0.3	------	13.
1 1215	-15	0.7560	------	------	------	------	------	8.5	------	4329.	------
1 1225	-5	------	------	------	------	------	------	------	------	------	------
1 1230	0	0.7440	0.7240	------	------	------	------	------	0.2	------	23.
1 1245	15	------	0.7350	0.0001	------	0.002	------	7.6	------	4244.	------
1 1300	30	0.7000	------	------	------	------	------	------	0.6	------	32.
1 1315	45	------	0.7110	------	------	------	------	7.1	------	4202.	------
1 1330	60	0.7000	------	------	------	------	------	------	0.0	------	33.
1 1345	75	------	0.6700	------	------	------	------	5.7	------	4103.	------
1 1400	90	0.6620	------	------	------	------	------	------	0.1	------	43.
1 1415	105	------	0.6580	0.0001	------	0.002	------	5.0	------	3976.	------
1 1430	120	0.6580	------	------	------	------	------	------	0.1	------	35.
1 1445	135	------	0.6560	------	0.0001	------	0.002	------	------	------	------

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NOX-HNO3 AIR IRRADIATION; EFFECT OF NH3
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CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 #PART>.5 PART/CC CLIMET	SIDE 2 #PART>.5 PART/CC CLIMET	SIDE 1 #PART>1 PART/CC CLIMET	SIDE 2 #PART>1 PART/CC CLIMET	SIDE 1 BSCAT 10-4 M-1 MRI 388	SIDE 2 BSCAT 10-4 M-1 MRI 388	SIDE 1 AER.V UM3/CC TSI 023	SIDE 2 AER.V UM3/CC TSI 023	SIDE 1 AER.N PART/CC TSI 023	SIDE 2 AER.N PART/CC TSI 023
1 1215	-15		1.		0.		0.3		0.		496.
1 1225	-5	2552.		371.		14.8		83.		1.1E 04	
1 1245	15		1.		0.		0.4		0.		574.
1 1300	30	2397.		300.		13.0		72.		9190.	
1 1315	45		1.		1.		0.4		1.		1441.
1 1330	60	2256.		251.		12.5		67.		8833.	
1 1345	75		1.		0.		0.4		2.		782.
1 1400	90	2115.		209.		11.0		61.		7223.	
1 1415	105		1.		0.		0.4		1.		940.
1 1430	120	1918.		158.		10.0		52.		7718.	
1 1445	135		2.		0.		0.4		1.		1207.

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 AER.S UM2/CC TSI 023	SIDE 2 AER.S UM2/CC TSI 023	SIDE 1 PART.024 PART/CC TSI 023	SIDE 2 PART.024 PART/CC TSI 023	SIDE 1 PART.042 PART/CC TSI 023	SIDE 2 PART.042 PART/CC TSI 023	SIDE 1 PART.075 PART/CC TSI 023	SIDE 2 PART.075 PART/CC TSI 023	SIDE 1 PART.133 PART/CC TSI 023	SIDE 2 PART.133 PART/CC TSI 023
1 1215	-15		14.		167.		87.		133.		72.
1 1225	-5	1432.		501.		1392.		977.		4483.	
1 1245	15		16.		167.		261.		0.		96.
1 1300	30	1225.		0.		1131.		932.		3856.	
1 1315	45		23.		1002.		174.		89.		120.
1 1330	60	1131.		167.		1044.		1288.		3374.	
1 1345	75		31.		334.		174.		133.		72.
1 1400	90	1023.		-501.		957.		977.		3085.	
1 1415	105		31.		334.		174.		222.		145.
1 1430	120	895.		835.		783.		1021.		2699.	
1 1445	135		24.		835.		0.		178.		121.

CLOCK TIME DY HR.	ELAPSED TIME (MIN)	SIDE 1 PART.237 PART/CC TSI 023	SIDE 2 PART.237 PART/CC TSI 023	SIDE 1 PART.422 PART/CC TSI 023	SIDE 2 PART.422 PART/CC TSI 023	SIDE 1 PART.750 PART/CC TSI 023	SIDE 2 PART.750 PART/CC TSI 023
1 1215	-15		37.		0.		0.
1 1225	-5	2927.		747.		126.	
1 1245	15		49.		0.		0.
1 1300	30	2571.		580.		119.	
1 1315	45		49.		7.		0.
1 1330	60	2288.		560.		112.	
1 1345	75		61.		0.		7.
1 1400	90	2103.		500.		102.	
1 1415	105		61.		0.		4.
1 1430	120	1845.		454.		81.	
1 1445	135		74.		0.		0.

------ NO DATA TAKEN

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NOX-HNO3 AIR IRRADIATION: EFFECT OF NH3
1980, OCT 22

NOTES

A   K1 CALCULATED FROM UV RADIOMETER DATA

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